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POLLUTANT SORPTION TO SOILS AND SEDIMENTS IN ORGANIC/AQUEOUS SOLVENT SYSTEMS

by

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16. ABSTRACT

The solubility and sorption properties of aromatic solutes in aqueous systems containing polar organic solvents were investigated. The work addressed the situation in which the release of hydrophobic organic contaminants as a result of a spill or accidental discharge may be accompanied by the release of water-soluble organic solvents. The investigation examined the effects of a polar solvent in water on the solubility of relatively hydrophobic solutes and the effect of polar solvent-water mixtures on sorption of organic solutes onto soil. The results are interpreted by means of chemical thermodynamic models to predict solubility in water/solvent systems and by semi-empirical models to correlate reduction in sorption characteristics with increase in solubility.

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FOREWORD

Environmental protection efforts are increasingly directed towards prevention of adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Chemistry Branch studies the chemical/biochemical reactions that control pollutant fate in soil and water ecosystems.

An understanding of the effect of a polar solvent in the aqueous phase on the physico-chemical properties of aromatic organic compounds is important in assessing the reactions and fates of these pollutants in heavily comtaminated aquatic and terrestrial systems. In the study reported here, the presence of a polar solvent in the aqueous phase was shown to have a significant effect on the solubility and soil sorption characteristics of hydrophobic aromatic solutes. Chemical thermodynamic models developed in the study may be used in predicting and assessing near-source transport of hydrophobic aromatic solutes in soil systems, in estimating aromatic solubility in heavily contaminated industrial wastewater, in evaluating solute properties for use in analytical procedures, and in other environmental applications.

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ABSTRACT

This report presents the results of an investigation to evaluate the solubility of relatively hydrophobic aromatic solutes in an aqueous phase containing a miscible polar organic solvent and to determine the effect of a polar solvent in the aqueous phase on the sorption of aromatic solutes onto soils. The investigation was comprised of both theoretical and experimental developments. The results from the solubility experiments were interpreted by means of chemical thermodynamic models to predict solute solubility in solvent/water systems, and the results of the soil sorption studies were evaluated by a model that relates reduction in sorption coefficient with increase in solubility.

The results of the investigation showed that hydrophobic aromatic solutes generally display a semi-logarithmic increase in solubility with increasing volume fraction of solvent in solvent/water mixtures. This results in a semi-logarithmic decrease in the tendency for these solutes to sorb onto soil. These findings were predicted by theory. However, an important result obtained from the sorption experiments was that the increase in solute solubility does not result in a directly proportional decrease in the sorption coefficient. This is believed to be the result of the solvent swelling the soil organic carbon material and thereby increasing the accessibility of the solute to this material. The increase in solute solubility in solvent/water mixtures and the decrease in sorption partition coefficients may be predicted by chemical thermodynamic models. This information is useful for assessing near-source transport of hydrophobic aromatic solutes in soil systems in the event of a spill or discharge of solutes with a polar solvent. The predictive techniques developed in this investigation may be useful in other applications in environmental engineering, such as for the estimation of aromatic solute solubility in heavily contaminated industrial wastewaters, or for evaluation of solute properties for use in analytical procedures.

The effect of solvent on the increase in solute solubility and the decrease in soil sorption is much more pronounced for the more hydrophobic solutes. Hence, the results of the investigation are particularly significant for assessment of reactions and fates for those aromatic compounds that exhibit lowest aqueous phase solubility.

This work was submitted in fulfillment of Cooperative Agreement No. CR810878 by Carnegie-Mellon University under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 1983 to June 1985, and work was completed as of June 1985.

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Chapter 1

INTRODUCTION

The purpose of this research is to evaluate the solubility of aromatic organic compounds in aqueous solutions containing a miscible polar solvent, and to determine the effect of a solvent in the aqueous phase on sorption of aromatic compounds onto soil. This study is comprised of both theoretical and experimental developments. The investigation was motivated by the need to understand the effect of polar solvent in the aqueous phase on physico-chemical properities of aromatic solutes. This is important for assessment of the reactions and fates of these types of pollutants in heavily contaminated systems.

It is shown in this investigation that the presence of polar solvent in the aqueous phase can have a significant effect on the solubility and soil sorption characteristics of hydrophobic aromatic solutes. These phenomena would be manifested wherever solvents and aromatic solutes are comingled, such as in wastewaters from chemical manufacturing processes or in concentrated hazardous/toxic wastes containing polar solvents or other water-soluble material. The effect of solvent on sorption of aromatic solutes onto soils is related to the evaluation of certain problems associated with groundwater contamination. This work addresses the situation for which near-source transport of hydrophobic aromatic solutes may be accompanied also by the release of water-soluble organic solvents, as in the case of spill or other discharge of concentrated wastes.

The investigation reports on results of experiments with various aromatic solutes including unsubstituted polycyclic aromatic compounds as well as polar, substituted aromatic compounds. This was done in order to represent a range of solute chemical properties including hydrophobicity, polarity and hydrogen bonding. The results from the solubility experiments are interpreted by means of chemical thermodynamic models to predict solute solubility in solvent/water systems. The results of the soil sorption studies are evaluated by a model which relates reduction in sorption partition coefficient to increased solute solubility in these systems.

This report begins with a chapter which provides a synthesis of available chemical thermodynamic techniques that may be used to estimate solute activity and solubility for nonelectrolytes in solvent/water systems. That chapter is followed by a discussion of experimental procedures and results of experiments which examine aromatic solute solubility in solvent/water mixtures. The next chapter evaluates and discusses several approaches to predict aromatic solute solubility in solvent/water systems. This evaluation considers a data set comprised of eighteen solute-solvent/water systems. The next chapter explains the development of a model to predict aromatic solute sorption onto soil in solvent/water mixtures. That chapter includes presentation of experimental results and a discussion of the model's appropriateness. The report concludes with a general summary of the results of the investigation.

Chapter 2

PREDICTION OF SOLUTE SOLUBILITY IN SOLVENT/WATER MIXTURES

This chapter summarizes several approaches which may be used to estimate solute solubility in solvent/water mixtures. These various approaches have a common theoretical basis in the thermodynamics of nonelectrolyte fluid-phase equilibria; however, the various approaches differ in the manner in which non-ideal effects are considered. It would be desired that the properties of a solution could be calculated from the properties of the pure components; unfortunately theoretical knowledge has not yet been developed to where this can be done with a degree of generality (Prausnitz, 1969). Therefore, it is necessary to rely upon experimental data to provide information on interaction parameters and other characteristics of real mixtures. Nonetheless, chemical thermodynamic techniques are useful for correlating data in a logical framework in order that predictions can be made about systems for which no data exist.

The following section introduces the subject of thermodynamics of fluids and defines several terms which are employed later. This is followed by a discussion of a procedure whereby an activity coefficient may be predicted from molecular structure, and this is followed by a discussion of estimation of activity coefficient in pure solvent. These subjects are then extended to predict solute solubility in binary solvent mixtures.

Phase Equilibria and Activity

This section reviews the concept of chemical potential for ideal and real solutions. The chemical potential of a real solution component is expressed in terms of fugacity, which is defined in terms of an activity coefficient and mole fraction of the solute. Relationships between activity coefficient and mole fraction are used for predicting solubility.

The solubility of a liquid or a solid solute in aqueous solution can be addressed by thermodynamics of phase equilibria. The principal thermodynamic function for describing phase equilibria at constant temperature was defined by Gibbs as the partial molar free energy, $\bar{G}_i$, or chemical potential, μ_i (Kcal/mole),

$$\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_j} \qquad (2\text{-}1)$$

where G is the Gibbs free energy, n_i is the moles of component i, P is pressure, T is temperature, and n_j is the mole numbers of all other components except i.

The equilibrium composition depends on various factors including temperature, pressure, and the chemical characteristics of the constituents of the system. The mathematical description of phase equilibria begins with the statement that at equilibrium the chemical potential of each component must be the same in each phase

$$\mu_i^{\alpha} = \mu_i^{\beta} \qquad (2\text{-}2)$$

where i refers to the ith component and α and β to the different phases. For purposes of engineering calculations, it is necessary to relate chemical potential to temperature, pressure, and mole fraction, X_i. This is facilitated by introducing certain other functions, namely activity and fugacity.

For pure liquids and pure solids, the chemical potential is the partial molar free energy, $\bar{G}_i$ (Kcal/mole), and it is a function of temperature and pressure alone. The value of the chemical potential for a pure component at a pressure of 1 atm is by convention referred to as the standard state chemical potential, $\mu°$. The relationship between chemical potential and pressure for n moles of pure gas (g) at constant temperature is derived from the ideal gas law (Prausnitz, 1969)

$$dG = V\ dP = nRT\ \frac{dP}{P} \tag{2-3}$$

Integrating from a standard pressure, P° to P, and recognizing for a one-component gas phase that the chemical potential is ΔG/n

$$\frac{G - G°}{n} = RT\ \ln \frac{P}{P°} = \mu(g) - \mu°(g) \tag{2-4}$$

where $\mu(g)$ is the chemical potential for the pure gas, V is the volume, R is the gas constant, T is the system temperature, and P is the pressure. If the standard pressure is taken as one atmosphere, and for an ideal mixture in which the chemical potential of each component behaves as if the other components were not present, then

$$\mu_i(g) = \mu_i°(g) + RT\ \ln P_i \tag{2-5}$$

where P_i is the partial pressure of the component i. The partial pressure is equal to the total pressure times the mole fraction of the component in the gas phase (Y_i), $P_i = Y_iP$, and Equation 2-5 can be expressed as

$$\mu_i(g) = \mu_i°(g) + RT\ \ln P + RT\ \ln Y_i \tag{2-6}$$

For an ideal solution, the chemical potential is defined in a manner similar to Equation 2-5 as for gases

$$\mu_i(sol) = \mu_i°(sol) + RT\ \ln X_i \tag{2-7}$$

where $\mu_i°(sol)$ is the standard state chemical potential and X_i is the mole fraction of component i in solution. For a solution in equilibrium with a vapor phase, the chemical potential in the liquid phase and gas phase are equal, and

$$\mu_i(\mathrm{sol}) = \mu_i(\mathrm{g}) \tag{2-8}$$

If the vapor phase is an ideal gas mixture, then

$$\mu_i^\circ(\mathrm{sol}) + RT \ln X_i = \mu_i^\circ(\mathrm{g}) + RT \ln P_i \tag{2-9}$$

This equation incorporates the relationship between Henry's law and Raoult's law. Raoult's law states that the ideal gas vapor pressure, P_i, of an ideal solution component is equal to the product of the vapor pressure of the pure liquid component, P_i° and the mole fraction of the component in solution, $P_i = X_i P_i^\circ$. Thus the standard state for a solution component depends on the ideal gas standard state, and the convention (Raoult's law) that $X_i = 1$ is the standard state for component i in solution. For real solutions, Raoult's law is obeyed as X_i approaches 1, and

$$\mu_i^\circ(\mathrm{sol}) = \mu_i^\circ(\mathrm{g}) + RT \ln P_i \tag{2-10a}$$

Henry's law states for an ideal component that the mole fraction in solution is proportional to the ideal gas partial pressure, $P_i = H_i X_i$. Comparison with Equation 2-10a shows that Henry's law constant is

$$H_i = \exp\left(\frac{\mu_i^\circ(\mathrm{sol}) - \mu_i^\circ(\mathrm{g})}{RT}\right) \tag{2-10b}$$

For real solutions, Henry's law is obeyed as $X_i \to 0$. Likewise, Equations 2-4 and 2-5 are valid only for ideal gas. In order to generalize the expressions, G. N. Lewis defined a function f, called fugacity, to describe the escaping tendency for any component in any system, whether solid, liquid, or gas, pure or mixed, ideal or non-ideal. For a real gas, the chemical potential of a component is expressed by an idealized pressure, called fugacity, f

$$\mu_i = \mu_i^\circ + RT \ln \frac{f_i}{f_i^\circ} \qquad (2\text{-}11)$$

where f_i° is the standard state fugacity: For a pure, ideal gas, the fugacity is equal to the pressure, and for a component i in a mixture of ideal gases, the fugacity is equal to its partial pressure. Since gas systems, pure or mixed, approach ideal gas behavior at low pressures, it is the convention that the standard state is taken as one atmosphere, for which the standard state fugacity of the component i usually approaches unity, and thus Equation 2-11 can be expressed as

$$\mu_i = \mu_i^\circ + RT \ln f_i \qquad (2\text{-}12)$$

The fugacity approaches the partial pressure of the component as the mixture becomes infinitely dilute (Stumm and Morgan, 1981). The relationship between fugacity and partial pressure may be expressed by a fugacity coefficient γ_{fi} (Prausnitz, 1969)

$$f_i = \gamma_{fi} P_i \qquad (2\text{-}13)$$

The fugacity coefficient is normally equal to unity for real gases at pressures in the range of one atmosphere.

For the case of real solutions, the chemical potential of a component is expressed by an idealized concentration called activity, a_i

$$\mu_i = \mu_i^\circ + RT \ln a_i \qquad (2\text{-}14)$$

The relationship between actual mole fraction, X_i, and activity is given by an activity coefficient, γ_i

$$a_i = \gamma_i X_i \qquad (2\text{-}15)$$

Hence, the chemical potential in real solutions is

$$\mu_i = \mu_i^\circ + RT \ln X_i + RT \ln \gamma_i \qquad (2\text{-}16)$$

The term RT $\ln\gamma_i$ describes the partial molar free energy of interactions that occur in non-ideal mixtures. The conventional definition of the reference state for a solvent, identified as component 1, is

$$\gamma_1 \rightarrow 1 \quad \text{as} \quad X_1 \rightarrow 1 \tag{2-17}$$

Thus for pure solvent, $\mu_1 = \mu_1^\circ$ when $a_1 = \gamma_1 X_1 = 1$. For a solute, identified as component 2, the reference state is the infinitely dilute solution. In general, $\gamma_2 > 1$ for a dilute solution of a given component in a given solvent. As the solution becomes increasingly dilute, the value of γ_2 approaches a limiting value, γ_2^∞, known as the infinite dilution activity coefficient (Prausnitz, 1969). Knowledge of the infinite dilution activity coefficient can be used to estimate solute solubility in water and in solvent/water mixtures. In addition, knowledge of the infinite dilution activity coefficient can be used to estimate other physico-chemical properties important to the environmental scientist, such as solvent/water partition coefficient and Henry's law constants (Grain, 1982; Campbell and Luthy, 1985).

The aqueous solubility of a hydrophobic organic compound in water or in water/polar solvent mixtures can be expressed in terms of fugacity using the Raoult's law convention

$$f = X\ \gamma f^R \tag{2-18}$$

where X is the mole fraction of the solute in solution, γ is the solute activity coefficient, and f^R is the reference fugacity, i.e., the fugacity of the pure compound at the system temperature. For liquid compounds f^R is the pure liquid compound vapor pressure, f^L. For solids, f^R is the extrapolated liquid fugacity below the triple point, f^s, not the solid fugacity or vapor pressure (Mackay, 1977; Prausnitz, 1969). Thus for liquids, $X = 1/\gamma$ since $f^R = f^L$, and for solids, $X = (f^s / f^R)/\gamma$. As explained below, the ratio (f^s / f^R) can be estimated by several standard procedures.

Activity Coefficient and Molecular Structure

Potentially, the most utilitarian approach towards prediction of chemical properties of mixtures is to base the approach on a description of the molecular structure of solvent and solute and to employ minimal chemical data. The following describes an approach of this type which has been developed in recent years to estimate activity coefficient in liquid mixtures. The approach was adapted to this investigation in order to estimate solute infinite dilution activity coefficient in pure solvent and in solvent/water mixtures.

The UNIFAC approach (UNIQUAC Functional Group Activity Coefficient) is a group contribution method for the prediction of activity coefficients of nonelectrolytes in liquid mixtures. The method combines a solution-of-functional-group concept with a model based on an extension of the quasi chemical theory (UNIQUAC) of liquid mixtures (Abrams and Prausnitz, 1975). The method is founded on the principle that group contribution concepts may be used to estimate thermodynamic properties of a liquid mixture, as first proposed by Langmuir (1925). Derr and Deal (1969) developed the analytical solution of groups (ASOG) method for correlating and predicting activity coefficients, and these concepts were incorporated by Fredenslund et al. (1975) in the UNIFAC method. Subsequently, the data base of the model has been extended (Gmehling et al. 1982) and applied to various problems including: estimating activity coefficients in organic solvent mixtures (Fredenslund et al. 1975), estimating the solubility of a solid in a solvent (Gmehling et al. 1978), evaluating the solubility of an aromatic hydrocarbon in various solvents (Martin et al. 1981), estimation of octanol/water partition coefficient (Arbuckle, 1983), predicting the solubility of chlorobenzenes in water (Benerjee, 1984), and estimating aromatic solute distribution coefficients for both polar and non-polar chemical compounds (Campbell and Luthy, 1985).

Estimation of Activity Coefficient by the UNIFAC Approach

The fundamental purpose of a solution-of-groups model is to utilize existing phase equilibria data for predicting phase equilibria of systems for which no experimental data are available. The UNIFAC model follows Derr and Deal's (1969) ASOG model which assumes that the logarithm of the activity coefficient is the sum of two parts --

- A combinatorial part that provides the contribution due to the difference of molecular size and shape of the molecule in the mixture, and
- A residual part that provides the contribution due to molecular interactions.

The combinatorial part is estimated by using the athermal Flory-Huggins equation (Flory, 1968), and the residual part is based on functional group interactions estimated by the Wilson equation (Wilson, 1962). The computational procedures employed in the UNIFAC model are reviewed below.

In a multicomponent mixture, the activity coefficient of component i can be expressed as

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R \tag{2-19}$$

where the first term represents the combinatorial contribution and the second term represents the residual contribution. The combinatorial part of Equation 2-19 can be expressed as

$$\ln \gamma_i^c = \ln \frac{\phi_i}{X_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{X_i} \sum_j X_j l_j \tag{2-20}$$

where the area fraction θ and the segment fraction ϕ are related to the mole fraction X through

$$\phi_i = \frac{r_i X_i}{\sum_j r_j X_j} \qquad \theta_i = \frac{q_i X_i}{\sum_j q_j X_j} \tag{2-21}$$

The pure-component molecular volume r_i and surface area q_i are given by group contributions R_k and Q_k as

$$r_i = \sum_k \nu_k^{\,i} R_k, \qquad q_i = \sum_k \nu_k^{\,i} Q_k \tag{2-22}$$

and

$$l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1) \tag{2-23}$$

In these expressions X_i is the mole fraction of component i, $\nu_k^{\,i}$ is the number of the functional groups of type k in component i, R_k is the van der Waals volume for functional group k, Q_k is the van der Waals surface area for functional group k, θ_i is the area fraction of component i, ϕ_i is the segment fraction which is similar to volume fraction of component i, and z is the coordination number, usually taken to be 10. The residual contribution of the activity coefficient is given by

$$\ln \gamma_i^R = \sum_k \nu_k^{\,i} \left[\ln \Gamma_k - \ln \Gamma_K^{\,i} \right] \tag{2-24}$$

where the group residual activity coefficient is related to composition and temperature through

$$\ln \Gamma_k = Q_k \left(1 - \ln \left[\sum_m \Theta_m \psi_{mk} \right] - \sum_m \left(\frac{\Theta_m \psi_{km}}{\sum_n \Theta_n \psi_{nm}} \right) \right) \tag{2-25}$$

In this expression Θ_m is the area fraction of group m over all groups

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}, \qquad X_m = \frac{\sum_j \nu_m^{\,j} X_j}{\sum_j \sum_n \nu_n^{\,j} X_j} \tag{2-26}$$

The group interaction parameter ψ_{mn} is given by

$$\psi_{mn} = \exp\left(-\frac{a_{mn}}{T}\right) \tag{2-27}$$

In the above expressions, Γ_k is the functional group-k residual activity coefficient, and $\Gamma_k^{\,i}$ is the residual activity coefficient of functional group-k in a reference solution containing only component i ($X_i = 1$). X_m is the mole fraction of functional group m, Θ_m is the surface area fraction of functional group m, and ψ_{mn} is the interaction parameter between functional group m and n. The parameter a_{mn} is a group interaction parameter which is a measure of the difference in interaction energy between group m and n. In general, a_{mn} is independent of temperature (Grain, 1982) and $a_{mn} \neq a_{nm}$. Considerable effort has been given to collecting and tabulating values of a_{mn}, R, and Q from experimental phase equilibrium data. The most up-to-date tabulation for a_{mn} is given by Gmehling et al. (1982).

Example calculations that demonstrate the use of the UNIFAC approach for estimating solute infinite dilution activity coefficient are provided in Appendix A.

Estimation of Infinite Dilution Activity Coefficient

The UNIFAC model can be used to predict infinite dilution solute activity coefficient (γ_2^{∞}) in water/co-solvent systems. A convenient methodology is to treat the solvent system as one component and the solute as a second component. The solvent system is treated as a single component in order to allow estimation of solute solubility from appropriate forms of the two- or three-suffix Margules equation as explained below. In this approach the solvent system may be envisioned as comprised of a "molecule" of water and co-solvent in proportion to the mole fraction water/co-solvent composition of interest. It does not matter if the "molecule" is comprised of water and co-solvent in non-integer ratios when using a solution-of-groups approach to estimate activity coefficients.

Estimating Solid Solute Solubility from Infinite Dilution Activity Coefficient

For the case of liquid solutes, mole fraction solubility in a solvent can be estimated readily as the reciprocal of the activity coefficient, provided the activity coefficient is sufficiently large. The situation is not as straight forward for estimation of the solubility of a solid solute (e.g. naphthalene) from knowledge of activity coefficient. This is because solubility depends not only on the activity coefficient but also on the fugacity of the standard state to which it is referred and on the fugacity of the pure solid (Prausnitz, 1969). If the solute is designated by the subscript 2, and if there is negligible solubility of the solvent in the solid, then at equilibrium

$$f_{2\,(\text{pure solid})} = f_{2(\text{solute in solution})} = \gamma_2\, X_2\, f_2^{\circ} \tag{2-28}$$

where f_2° is the standard state fugacity to which the liquid-phase activity coefficient, γ_2, refers. The mole fraction solubility can be calculated from the activity coefficient and the ratio of the fugacities in the solid phase and the standard state. For many solids the vapor pressure of the pure solid and the vapor pressure of the subcooled liquid is not large. Also the pure solute activity coefficient can be assumed as unity, and thus the vapor pressures of the pure solid and the subcooled liquid can be substituted as an approximation for calculating solute solubility (Prausnitz, 1969)

$$X_2 = \frac{f_{2(\text{pure solid})}}{\gamma_2 f_2^{\circ}} = \frac{P^{s}_{2\,(\text{pure solid})}}{P^{s}_{2\,(\text{pure subcooled liquid})}} \tag{2-29}$$

The standard state fugacity for solids is usually defined by convention as the fugacity of pure, subcooled liquid at the temperature of the solution at a specified pressure. Although this is a hypothetical standard state, it is one for which properties can be calculated provided that the solution temperature is not very far removed from the triple point of the solute (Prausnitz, 1969; Mackay and Shiu, 1977).

An expression for the ideal solubility of a solid solute in a liquid solvent is given by Equation 2-29, but a method still needs to be given for finding the saturation pressure for the subcooled liquid. This can be achieved by assuming that the solution is ideal. Then $\gamma_2 = 1$ and the solubility can be expressed as (Prausnitz, 1969)

$$\ln \frac{1}{\gamma_2\, X_2} = -\ln \left(\frac{f_{2(\text{pure solid})}}{f_2^{\circ}}\right)$$

$$= \frac{\Delta H_f}{RT}[1 - \frac{T}{T_t}] - \frac{\Delta C_p}{R}\left(\frac{T_t - T}{T}\right) + \frac{\Delta C_p}{R}\ln\frac{T_t}{T} \qquad (2\text{-}30)$$

where ΔC_p is the difference of specific heat between solid and liquid, ΔH_f is the enthalpy of fusion for the solid in units of cal/mole at the triple point temperature, and T_t is the triple-point temperature, °K.

Two simplifications in Equation 2-30 are frequently made but these usually introduce only a slight error (Prausnitz,1969). First, for most chemical compounds there is little difference between the triple-point temperature and the normal melting temperature; also the difference in the heat of fusion, ΔH_f, at these two temperatures is often negligible. Therefore, in practice the melting temperature can be used to substitute for the triple-point temperature, and ΔH_f at the melting temperature can be used for heat of fusion at the triple-point. Secondly, the three terms on the right hand side of Equation 2-30 are not of equal importance; the first term is the dominant one and the remaining two, being of opposite sign, have a tendency to cancel each other, especially if T and T_t are not far apart (Prausnitz,1969). Therefore in many cases it is sufficient to consider only the first term which includes ΔH_f, and Equation 2-30 becomes

$$\ln \gamma_2 X_2 = \ln [\frac{f_{2(\text{pure solid})}}{f_2^{\circ}}] = \frac{\Delta H_f}{RT}[\frac{T}{T_m} - 1] \qquad (2\text{-}31)$$

where T is the system temperature in °K, T_m is the melting temperature of the pure solid in °K, R is the gas constant, 1.987 cal/mole °K, and ΔH_f is the enthalpy of fusion for the solid in cal/mole, at the melting point. A comparison of use of Equations 2-30 and 2-31 to estimate mole fraction solubility from activity coefficient is presented in Chapter 4.

Equation 2-31 employs heat of fusion, which is usually close to heat of solution for a solid (Prigogine and Defay, 1973). It may be concluded from Equation 2-31 that ideal solubility of a solid solute in a liquid solvent increases with temperature. Also, at a given temperature the solid with the lower melting temperature will have the greater solubility among solids with similar enthalpy of fusion, and likewise, among solids with similar melting temperatures, the solid with the lowest enthalpy of fusion will exhibit the greater solubility.

Hildebrand (1950) proposed that the heat of fusion at temperature T can be calculated from the heat of fusion at the melting point, $\Delta H_{f,m}$, and the molal heat capacity of the solute as liquid ($C_{p,l}$) and as solid ($C_{p,s}$)

$$\Delta H_f = \Delta H_{f,m} - (C_{p,l} - C_{p,s})\,(T_m - T) \qquad (2\text{-}32)$$

This expression can be used to compensate in part for the error introduced by omission of ΔC_p terms in the simplified fugacity ratio expression given by Equation 2-31. Heat capacity data are available for only a few solid solutes; for example, these data were available for two of the aromatic solutes of interest in this investigation. Fortunately, the $\Delta H_{f,m}$ term is dominant in Equations 2-31 and 2-32 and it is sufficient in most cases to neglect corrections which depend on ΔC_p (Prausnitz, 1969). Furthermore, Gmehling et al. (1978) also noted that the required C_p data are usually not available, and that these corrections are small compared to other uncertainties in estimation of the activity coefficient.

Enthalpy of fusion and melting temperature for many of the solutes considered in this investigation are available in standard references (Weast, 1983). In those cases for solid solutes for which these data are not available, heat of fusion may be calculated from entropy of fusion, ΔS_f, [cal/°K mole], as

$$\Delta H_f = \Delta S_f\, T_m \qquad (2\text{-}33)$$

As discussed later, ΔH_f was calculated according to Equation 2-32 if appropriate heat capacity data for the solid and liquid phase were available. If no ΔC_p data were available, $\Delta H_{f,m}$ was used as ΔH_f in Equation 2-31 without correction. If no data on $\Delta H_{f,m}$ were available, then the heat of fusion of the solute was estimated according to Equation 2-33. Various researchers have reported for many moderately-sized organic molecules, including substituted aromatic hydrocarbons, that entropy of fusion is nearly constant at about 13 to 13.5 cal/mole °K (Tsonopoulos and Prausnitz, 1971; Yalkowsky, 1979). Thus Equations 2-31 and 2-33 can be reduced to the following expression by assuming ΔS_f is constant at 13 cal/mole °K

$$\ln \gamma_2 x_2 = 6.56 \left(\frac{T-T_m}{T}\right) \qquad (2\text{-}34)$$

Yalkowsky (1981) has discussed the assumptions in simplification of Equation 2-30 in which the mole fraction solubility of the crystalline solute (X^c) and the subcooled liquid X^{scl} may be given as either

$$\ln \left(\frac{X^c}{X^{scl}}\right) = -\frac{\Delta S_f}{RT}(T_m-T) \qquad (2\text{-}35)$$

or

$$\ln \left(\frac{X^c}{X^{scl}}\right) = -\frac{\Delta S_f}{R}\ln \left(\frac{T_m}{T}\right) \qquad (2\text{-}36)$$

Equation 2-35 results from the assumption that $\Delta C_p = 0$, while Equation 2-36 results from the assumption that $\Delta C_p = \Delta S_f$. In an ideal solution, the solute-solute and solvent-solvent interactions are equivalent to the solute-solvent interactions, and there is no change in heat or volume on mixing. This results in infinite miscibility of a solute, or the ideal mole fraction solubility of the solute can be assumed as unity, $X^{scl} = 1$. It was demonstrated by Yalkowsky for polycyclic aromatic hydrocarbons at room temperature (300 °K) with melting points less than about 100 °C (e.g. naphthalene, acenaphthene, fluoranthene, flourene, and phenanthrene) that there was little difference between Equations 2-35 and 2-36, as both equations showed good correlation for solubility of fourteen polycyclic compounds in benzene. However, Equation 2-35 was recommended because a value of the entropy of fusion which could be calculated from the data was closer to an expected value of about 13 cal/mole °K. Also, Equation 2-35 is analogous to Equation 2-31.

In this investigation UNIFAC was used to estimate solute infinite dilution activity coefficient in various systems, γ_2^{∞}. For those cases in which $\gamma_2^{\infty} > 100$, Equation 2-31 can be used to estimate solute mole fraction solubility for solids

$$\ln \gamma_2^{\infty} X_2 = \frac{\Delta H_f}{RT} \left(\frac{T}{T_m} - 1\right) \qquad (2\text{-}37)$$

However, if γ_2^{∞} is < 100, then the mole fraction solubility calculation must recognize that at infinite dilution there is appreciable solubility of solute, and solvent mole fraction does not approach unity. Lyman (1982) suggests that if $10 < \gamma_2^{\infty} < 100$, the solubility of solute may be described by the two-suffix Margules equation

$$\ln X_2 + (1 - X_2)^2 \ln \gamma_2^{\infty} = \frac{\Delta H_f}{RT} \left(\frac{T}{T_m} - 1\right) \qquad (2\text{-}38)$$

where X_2 is obtained from trial and error solution of Equation 2-38. If $\gamma_2^{\infty} < 10$, the recommended procedure is to estimate several values of γ_2^{∞} at corresponding values of X_2 and to plot γ_2^{∞} versus X_2. Then using matched values of γ_2^{∞} and X_2, search for a value of $\ln (\gamma_2^{\infty})$ that equals $(\Delta H_f/RT) (\frac{T}{T_m} - 1)$. UNIFAC can be used to estimate values of γ_2^{∞} for different values of X_2, and thus the mole fraction solubility is given by the value of X_2 which satisfies Equation 2-37. If no value of X_2 satisfies Equation 2-37, then it may concluded that the solute and solvent are miscible at the system temperature, T.

Estimating Liquid Solute Solubility from Infinite Dilution Activity Coefficient

For the case of liquid solutes, mole fraction solubility is estimated from γ_2^{∞} as follows. If $\gamma_2^{\infty} > 1000$, the solubility of solute can be estimated by

$$X_2 = \frac{1}{\gamma_2^{\infty}} \qquad (2\text{-}39)$$

If $50 < \gamma_2^{\infty} < 1000$, then X_2 is calculated from the following equation by trial and error with $X_2 = \frac{1}{\gamma_2^{\infty}}$ as the initial approximation (Lyman, 1982)

$$(1 - 4X_2 + 3x_2^2)\ \ln\gamma_2^{\infty} + (2x_2 - 3x_2^2)\ \ln\gamma_1^{\infty} + \ln X_2 - \ln(1-x_2) = 0 \qquad (2\text{-}40)$$

If $7.4 < \gamma_2^{\infty} < 50$, then UNIFAC is used to estimate several values of γ_1 and γ_2 at corresponding values of X_1 and X_2. Then the Gibbs free energy of mixing, $(\Delta G^M/ RT)$, is calculated as a function of component mole fraction (X_1, X_2) and component activity coefficients (γ_1, γ_2)

$$\frac{\Delta G^M}{RT} = X_1 \ln \gamma_1 + X_2 \ln \gamma_2 + X_1 \ln X_1 + X_2 \ln X_2 \qquad (2\text{-}41)$$

Values of $\frac{\Delta G^M}{RT}$ are then plotted on the ordinate versus X_2 on the abscissa. If two phases are predicted, a curve with two minima will result; if only one minima is obtained, then the two liquids may be assumed to be miscible in all proportions. In the case of a curve with two minima, a straight line may be drawn simultaneously tangent to the curve at the two minima. The points of tangency correspond to the solubility limits for solvent in solute and solute in solvent (Lyman, 1982).

If $\gamma_2^{\infty} < 7.4$, the two liquids can be assumed to be completely miscible at the system temperature.

Prediction of Solute Solubility in Mixed Solvent Systems by Use of an Excess Free Energy Approach

The following derivation explains a relationship between solute activity coefficient, solute Henry's law constant in pure solvent, and solute-free solvent volume fractions. This relationship (Equation 2-57) is then used with an expression for the excess Gibbs free energy of mixing to estimate the solubility of a solute in a mixed solvent system (Equation 2-73). The theoretical development described below follows the approach of Williams and Amidon (1984a). In the following, subscript 1 refers to co-solvent, subscript 2 refers to solute, and subscript 3 refers to water.

For a solute in equilibrium with its solid phase, the fugacity of the solute in solution is given from Equation 2-18

$$\gamma_2 X_2 f_2^{o} = f_{2\ (\text{pure solid})} = f_2^{s} \qquad (2\text{-}42)$$

where f_2^{o} is simplified notation for the fugacity of the hypothetical pure liquid solute at the same temperature T and pressure P as the solution ($f_{2\ (\text{pure, subcooled liquid})}$), and f_2^{s} is a simplified notation for the fugacity of the solute in the liquid solution

$$f_2^{s} = f_{2\ (\text{solute in liquid solution})} \qquad (2\text{-}43)$$

The solute activity coefficient, γ_2, has been defined according to the symmetric or Raoult's law convention for which $\gamma_2 \rightarrow 1$ as $X_2 \rightarrow 1$. As X_2 approaches zero, γ_2 becomes

$$\gamma_2^{\infty} = \lim_{x_2 \to 0} \gamma_2 \qquad (2\text{-}44)$$

and the mole fraction solubility limit is given as

$$\ln X_2 = \ln \left(\frac{f_2^{s}}{f_2^{o}}\right) - \lim_{x_2 \to 0} \ln \gamma_2 \qquad (2\text{-}45)$$

This condition may be expressed by Henry's law as

$$\lim_{x_2 \to 0} \frac{f_2^{s}}{x_2} = H_2 \qquad (2\text{-}46)$$

where H is Henry's law constant. If the mole fraction solubility of solute in solution is sufficiently small such that Henry's law holds, then

$$f_2^{s} = f_{2(\text{pure solid})} = H_2X_2 \qquad (2\text{-}47)$$

If Equation 2-46 is expressed in logarithms, and if the expression is written for solvents, as indicated by subscripts 1 for the organic co-solvent and subscript 3 for water, and subscript 2 for solute, then for the organic co-solvent

$$\lim_{x_2 \to 0} \ln \gamma_{2,1} = \ln \frac{H_{2,1}}{f_2^{o}} \qquad (2\text{-}48)$$

and for solvent 3, water

$$\lim_{x_2 \to 0} \ln \gamma_{2,3} = \ln \frac{H_{2,3}}{f_2^{o}} \qquad (2\text{-}49)$$

and for a binary mixture of solvents 1 and 3, as indicated by a subscript m

$$\lim_{x_2 \to 0} \ln \bar{x}_{2,m} = \ln \frac{H_{2,m}}{f_2^{o}} \qquad (2\text{-}50)$$

Combining Equations 2-45 and 2-48 to 2-50 gives expressions for mole fraction solubility, X^{s}, of component 2 in terms of Henry's law constant and solute fugacity in solution

$$\ln x_{2,1}^{s} = \ln \frac{f_2^{s}}{H_{2,1}}; \qquad \ln f_2^{s} = \ln x_{2,1}^{s} + \ln H_{2,1} \qquad (2\text{-}51)$$

$$\ln x_{2,3}{}^{s} = \ln \frac{f_2{}^{s}}{H_{2,3}}; \qquad \ln f_2{}^{s} = \ln x_{2,3}{}^{s} + \ln H_{2,3} \tag{2-52}$$

$$\ln x_{2,m}{}^{s} = \ln \frac{f_2{}^{s}}{H_{2,m}}; \qquad \ln f_2{}^{s} = \ln x_{2,m}{}^{s} + \ln H_{2,m} \tag{2-53}$$

The volume fraction, z_i, of any component in the mixture is computed from component mole fraction as

$$z_i = \frac{X_i\ q_i}{\sum_j X_j\ q_j} \qquad \text{and} \qquad \sum_i z_i = 1 \tag{2-54}$$

where q_i is the molar volume for component i, which is calculated as component molecular weight divided by component density. It is convenient to define terms with respect to solute-free volume fraction, i.e. for which $X_2 \to 0$ and thus $z_2 \to 0$, and in this case

$$\bar{z}_1 + \bar{z}_3 = 1 \tag{2-55}$$

where the circumflex denotes solute-free terms. If Equation 2-51 is multiplied by $\bar{z}_1$ and Equation 2-52 is multiplied by $\bar{z}_3$, and the two resulting equations are combined, then

$$\ln f_2{}^{s} = \bar{z}_1 (\ln X_{2,1}{}^{s} + \ln H_{2,1}) + \bar{z}_3 (\ln X_{2,3}{}^{s} + \ln H_{2,3}) \tag{2-56}$$

Substitution of Equation 2-53 into Equation 2-56 results in

$$\ln X_{2,m}{}^{s} = \bar{z}_1 \ln X_{2,1}{}^{s} + \bar{z}_3 - (\ln H_{2,m} - \bar{z}_1 \ln H_{2,1} - \bar{z}_3 \ln H_{2,3}) \tag{2-57}$$

For a multicomponent mixture, Equation 2-57 may be expressed as

$$\ln X_{2,m}{}^{s} = \sum_i \bar{z}_i \ln X_{2,i}{}^{s} - (\ln H_{2,m} - \sum_i \bar{z}_i \ln H_{2,i}) \tag{2-58}$$

Equation 2-58 states that the solubility of solute in a solvent mixture is a volume fraction weighted sum of the pure solvent solubilities plus a term which may be called an excess Henry's law constant. Williams and Amidon (1982a) employed an excess free energy model as proposed by Wohl (1946) to develop an expression for the excess Henry's law constant. This is explained below.

In a homogeneous multicomponent system, the total free energy, G, can be expressed in terms of each component i

$$G = \sum_i n_i G_i^\circ + RT \sum_i n_i \ln X_i + \left(\sum_i n_i \right) \Delta G \tag{2-59}$$

where n_i is the number of moles for component i, G_i° is the free energy per mole of pure component i, and ΔG is the excess free energy per mole of this mixture. The first term in Equation 2-59 represents the contribution of free energy of each of the pure components, the second term represents the free energy of ideal mixing, and the third term represents the excess free energy from nonideal mixing. The partial molar free energy of component j in the mixture at constant temperature, T, and constant pressure, P, can be expressed as

$$\left(\frac{\partial G}{\partial n_j} \right)_{T,P} = G_j + RT \ln X_j + RT \ln \gamma_j \tag{2-60}$$

where

$$\ln \gamma_j = \left(\frac{\partial [\sum_{i=1} n_i \, \Delta G/RT]}{\partial n_j} \right)_{T,P,n_{i \neq j}} \tag{2-61}$$

The excess free energy in a three component mixture can be expressed in a general form as (Wohl, 1946)

$$\begin{aligned} \frac{\Delta G}{2.3RT\ (q_1x_1 + q_2x_2 + q_3x_3)} &= 2a_{12}z_1z_2 + 2a_{13}z_1z_3 + 2a_{23}z_2z_3 \\ &+ 3a_{112}z_1^2z_2 + 3a_{122}z_1z_2^2 + 3a_{113}z_1^2z_3 \\ &+ 3a_{133}z_1z_3^2 + 3a_{223}z_2^2z_3 + 3a_{233}z_2z_3^2 \\ &+ 6a_{123}z_1z_2z_3 \end{aligned} \tag{2-62}$$

where $z_i = \frac{x_i \, q_i}{\Sigma \, x_i \, q_i}$, and q values are molar volume, and the "a" terms are interaction parameters between molecules. For example a_{12} is the interaction parameter between one molecule of component 1 and one molecule of component 2, a_{113} is the interaction parameter for three interacting molecules comprised of two molecules of component 1 and one molecule of component 3. The numerical coefficient and the volume fraction parameters in each of the terms in Equation 2-62 relate to the probability of interaction, i.e. $(2z_1\ z_2)$ is the probability that any two molecules consisting of one molecule each of components 1 and 2 will interact (Prausnitz, 1969). Equation 2-62 is referred to as a three suffix equation, i.e. a solute or solvent molecule is considered as interacting with no more than two other bodies. Higher or lower suffix equations may be written if it is desired to consider fewer or more body interactions. Wohl (1946) and Wilson and Amidon (1984a) simplified Equation 2-62 by defining

$$
\begin{aligned}
A_{2\text{-}1} &= q_2(2a_{12} + 3a_{112}) \\
A_{3\text{-}1} &= q_3(2a_{13} + 3a_{113}) \\
A_{2\text{-}3} &= q_2\ (2a_{23} + 3a_{233}) \\
A_{1\text{-}2} &= q_1(2a_{12} + 3_{a122}) \\
A_{1\text{-}3} &= q_1(2a_{13} + 3_{a133}) \\
A_{3\text{-}2} &= q_2(2a_{32} + 3_{a223}) \\
C_1 &= q_1\ [3a_{112} + 3a_{133} + 3a_{223} - 6a_{123}] \\
C_2 &= q_2\ [3a_{112} + 3a_{133} + 3a_{223} - 6a_{123}] \\
C_3 &= q_3\ [3a_{112} + 3a_{133} + 3a_{223} - 6a_{123}]
\end{aligned}
$$

Substitution of these expressions into Equation 2-62 and differentiation results in an expression for solute activity coefficient in a mixture of binary solvents.

$$\left(\frac{\partial n_T \Delta G/RT}{\partial n_2}\right)_{T,P,n_1,n_3} = \ln \gamma_{2,m}$$

$$= z_3^2[A_{2-3}+2z_2(A_{3-2}\frac{q_2}{q_3}-A_{2-3})]+z_1^2[A_{2-1}+2z_2(A_{1-2}\frac{q_2}{1}-A_{2-1})]$$

$$+ z_1z_3[A_{3-2}\frac{q_2}{q_3}+2z_2(A_{1-2}\frac{q_2}{q_3}-A_{2-1})] - 2z_1[A_{1-3}\ \frac{q_2}{q_1} - A_{3-1}\frac{q_2}{3}]$$

$$- C_2\ (2-3z_2) - C_3\frac{q_2}{q_3}z_3(1-3z_2) - C_1\frac{q_2}{q_1}z_1(1-3z_2)$$

(2-63)

When the solution is infinitely dilute $X_2 \rightarrow 0$ and $z_2 \rightarrow 0$ and Equation 2-63 can be simplified as

$$\ln\ \gamma_{2,m} = \bar{z}_3^{\,2}A_{2-3} + \bar{z}_1^{\,2}A_{2-1} + \bar{z}_1\ \bar{z}_3[A_{3-2}\frac{q_2}{q_1} + A_{2-1} - A_{1-3}\frac{q_2}{q_1}$$

$$+ 2\bar{z}_1(A_{1-3}\frac{q_2}{q_1} - A_{3-1}\frac{q_2}{q_3} - C_3\frac{q_2}{q_3}z_3 - C_1\frac{q_2}{q_1}z_1)] \qquad (2\text{-}64)$$

Further simplification of Equation 2-64 is obtained by recognizing that

$$C_2 = C_1\ \frac{q_2}{q_1}, \qquad \text{and} \qquad C_3 = C_1\ \frac{q_2}{q_1} \qquad (2\text{-}65)$$

It may also be assumed that the following interactions are similar (Williams and Amidon, 1984a)

$$a_{122} \cong a_{112}, \qquad \text{and} \qquad \frac{A_{1-2}}{A_{2-1}} = \frac{q_1}{q_2} \qquad (2\text{-}66)$$

$$a_{233} \cong a_{223}, \qquad \text{and} \qquad \frac{A_{2-3}}{A_{3-2}} = \frac{q_2}{q_3} \qquad (2\text{-}67)$$

Substitution of these expressions into Equation 2-64 results in

$$\ln\ \gamma_{2,m} = \bar{z}_3A_{2-3} + \bar{z}_1A_{2-1} + A_{1-3}\ \bar{z}_1\ \bar{z}_3(2\ \bar{z}_1-1)\ \frac{q_2}{q_1}$$

$$+ 2A_{3-1}\ \bar{z}_1^{\,2}\ \bar{z}_3\ \frac{q_2}{q_3} - C_2z_1z_3 \qquad (2\text{-}68)$$

Comparison of the first two terms on the right hand side of Equation 2-68 with Equations 2-48 and 2-49 shows

$$\lim_{x_2 \to 0} \ln \gamma_{2,1} = \ln \frac{H_{2,1}}{f_2^{\circ}} = A_{2-1} \tag{2-69}$$

$$\lim_{x_2 \to 0} \ln \gamma_{2,3} = \ln \frac{H_{2,3}}{f_2^{\circ}} = A_{2-3} \tag{2-70}$$

$$\lim_{x_2 \to 0} \ln \gamma_{2,m} = \ln \frac{H_{2,m}}{f_2^{\circ}} \tag{2-71}$$

Therefore

$$\begin{aligned} \ln H_{2,m} = {} & \bar{z}_1 \ln H_{2,1} + \bar{z}_3 \ln H_{2,3} + A_{1-3}\, \bar{z}_1 \bar{z}_3\, (2\bar{z}_1 - 1) \frac{q_2}{q_1} \\ & + 2A_{3-1} \bar{z}_1^{\,2}\, \bar{z}_3 \frac{q_2}{q_3} - C_2 z_1 z_3 \end{aligned} \tag{2-72}$$

Substitution of Equation 2-72 into Equation 2-57 results in an expression for solute solubility in a binary solvent mixture

$$\begin{aligned} \ln X_{2,m} = {} & \bar{z}_1 \ln X_{2,1}^{\,s} + \bar{z}_3 \ln X_{2,3}^{\,s} + A_{1-3} \bar{z}_1 \bar{z}_3\, (2\bar{z}_1 - 1) \frac{q_2}{q_1} \\ & + 2A_{3-1} \bar{z}_1^{\,2} \bar{z}_3 \frac{q_2}{q_3} - C_2 z_1 z_3 \end{aligned} \tag{2-73}$$

Equation 2-73 expresses the solubility of solute (2) in a binary mixed solvent (components 1 and 3). The first two terms of Equation 2-73 represent the solubility of solute in pure solvents. The next two terms represent the contribution of solvent-solvent interactions, and the last term of Equation 2-73 accounts for the interaction between solute and solvent. This term is essentially a ternary correction parameter.

Several input data are needed in order to estimate solute solubility in a multicomponent system through use of Equation 2-73,

- Solute solubility in pure solvents, ($X_{2,1}^{\,s}$ and $X_{2,3}^{\,s}$);
- Solvent-solvent interaction constants, A_{3-1} and A_{1-3}; and
- Solute-solvent interaction constant, C_2.

Application of Equation 2-73 requires various information as listed above.

Some of these information needs can be estimated by use of the UNIFAC model. Equation 2-73 was employed in this investigation by using UNIFAC estimates of solvent activity coefficients to predict solute solubility in pure solvent and/or to predict the solvent-solvent interaction constants (A_{1-3} and A_{3-1}). These procedures are discussed below.

Solubility of a solute in a pure organic co-solvent can be obtained either from literature (Weast, 1983, Stephen and Stephen, 1963), or estimated from the procedures described in the previous section. It is noted that while solute solubility in water may be available for various aromatic solutes, comparatively little information is available on solute solubility in common organic co-solvents. The solvent-solvent interaction constants (A_{1-3} and A_{3-1}) are independent of solute, and they can be estimated from activity coefficient, molar volume and solute-free volume fractions of the solvents. If the mole fraction of the solute is near zero ($X_2 \rightarrow 0$), the volume fraction of the solute is close to zero ($z_2 \rightarrow 0$), and by applying the definition of A_{1-3} and A_{3-1} into Equation 2-73, the molar excess free energy is given as (Williams and Amidon, 1984b)

$$\frac{\Delta G}{RT} = \frac{A_{1-3}}{q_1}[\bar{z}_1\bar{z}_3^{2}(X_1q_1 + X_3q_3)] + \frac{A_{3-1}}{q_3}[\bar{z}_1^{2}\bar{z}_3(X_1q_1 + X_3q_3)] \qquad (2\text{-}74)$$

also

$$\frac{\Delta G}{RT} = \sum_i X_i \ln \gamma_i = X_1 \ln\gamma_1 + x_3 \ln \gamma_3 \qquad (2\text{-}75)$$

and thus

$$X_1 \ln\gamma_1 + X_3 \ln\gamma_3 = \frac{A_{1-3}}{q_1}[\bar{z}_1\bar{z}_3^{2}(X_1q_1 + X_3q_3)] + \frac{A_{3-1}}{q_3}[\bar{z}_1^{2}\bar{z}_3(X_1q_1 + X_3q_3)] \qquad (2\text{-}76)$$

Equation 2-73 was used in this investigation to predict solute solubility in water/co-solvent system. This was done by using Equation 2-76 from which the constants A_{1-3} and A_{3-1} may be computed from knowledge of solvent activity coefficients. The solvent activity coefficients (γ_1 and γ_3) for different co-solvent/water compositions were estimated by the UNIFAC method. $\bar{z}_1$ and $\bar{z}_3$ were calculated from Equation 2-54, and hence the constants A_{1-3} and A_{3-1} were obtained by statistical regression of two parameters. In this investigation the two parameter statistical regression procedure was performed according to the techniques described by Ryan et al. (1981).

Williams and Amidon (1984b) employed Equations 2-73 and 2-76 to describe the solubility of ten compounds in ethanol/water mixtures. In their study the solvent-solvent interaction parameters were determined from estimation of activity coefficient using partial pressure data for ethanol/water mixtures. The constant C_2 accounts for interaction between solute and the two solvents, and Williams and Amidon (1984b) estimated C_2 by linear regression of the difference between the experimental solubility and calculated solubility without the C_2 term using Equation 2-73. The C_2 terms were obtained in this fashion for ten compounds of interest in pharmaceutical science, such as acetanilide, barbituric acid, antipyrine, and phenobarbital. Williams and Amidon (1984b) noted that in principle it is possible to obtain the constant C_2 from only one or two observations on solute solubility in a dual solvent system. They observed that Equation 2-73 adequately described the systems investigated except for antipyrine which was not as well characterized by Equation 2-73. This was attributed to antipyrine having very high solubility in both solvents which invalidated the assumptions made in deriving Equation 2-73; that is, the assumption that the solubility of solute was small. It was noted by these investigators that the solvent-solvent interaction constants in combination with the ideal mixture solubilities tended to overpredict for nonpolar compounds and underpredict for polar solutes, hence C_2 was usually of opposite sign to the sum of the solvent-solvent terms. It was also noted that the C_2 term could be related to the polar or nonpolar nature of the solute by correlation of C_2 with solute octanol-water partition coefficient, K_{ow}. For eight solutes and ethanol-water mixtures C_2 was correlated with K_{ow} as

$$C_2 = -3.96 - 2.66 \log K_{ow} \qquad r = 0.95 \qquad (2\text{-}77)$$

This correlation suggests that it may be possible to estimate C_2 from octanol-water partition coefficient data, and then use an estimated C_2 term in conjunction with the solvent-solvent terms and pure solvent solubilities to predict the solute solubility-solvent composition profile.

Williams and Amidon (1984c) refer to Equation 2-73 as a reduced three-suffix solubility equation, as developed from an excess free energy model proposed by Wohl (1946). In additional work they obtained experimental vapor pressure-solvent composition data for ethanol-propylene glycol and propylene glycol-water systems to estimate binary solvent interaction constants (the "A" terms) in order to describe phenobarbital solubility in these solvent mixtures. It was found that the three suffix excess free energy model predicted solute solubility for the binary solvent systems. It was concluded that a log-linear solubility relationship is observed when the solvent interaction constants (the A terms) are small compared to the interaction between solute and solvent mixture (as estimated by C_2). Thus, the solubility of a solute in propylene glycol-water mixtures showed an approximate semi-logarithmic relationship between solubility and volume fraction propylene glycol because solubility may be described from a volume fraction weighted sum of the pure solvent solubilities and a solute-solvent interaction term.

It was concluded that the three-suffix equation was well suited for the systems for which it was derived, as for solutes with low solubility in water or other solvent. It was judged that for pharmaceutical purposes this was not a restriction, as compounds that demonstrate high solubility in a solvent such as water do not require a second, or co-solvent, to increase their solubility for administration of pharmaceutical chemicals.

Prediction of Solute Solubility in Mixed Solvents by Log-Linear Relationships

Yalkowsky et al. (1972) reported on the solubility of alkyl p-aminobenzoates in water-propylene glycol mixtures, and found that the solubility could be described by a semi-logarithmic relationship

$$\log S = \log S_w + \sigma z \tag{2-78}$$

where S is the solute solubility in moles/l, S_w is the solute solubility in water, z is the volume fraction of co-solvent, and σ is a parameter which was characteristic of the system under study. Later it was reported by Yalkowsky and Flynn (1974) that the solubility of p-aminoacetophenone in water-propylene glycol mixtures required Equation 2-78 to be expanded to a fifth-degree polynomial in z in order to account for nonlinearity of solubility with increasing fraction of propylene glycol. Equation 2-78 has been discussed by Martin et al. (1982) where it was noted that it was applicable to systems where the polarity of the drug was significantly less than either of the solvents in the binary mixtures. It was shown (Martin et al. 1982) that the linear dependence of logarithmic solubility on volume fraction of the co-solvent was applicable when the Hildebrand solubility parameter of solvents were 3 or more solubility units larger than the solubility parameter of the solute.

The Hildebrand solubility parameter, δ, in units of $(\text{cal/cm}^3)^{1/2}$ is defined as the square root of the pure liquid component cohesive energy density, C,

$$\delta = C^{1/2} = \left(\frac{\Delta U}{\Delta V}\right)^{1/2} \tag{2-79}$$

where ΔU is the energy required to isothermally evaporate liquid to gas, cal/mole, and V is the liquid molar volume, [cm^3/mole]. At temperatures below the critical temperature

$$\Delta U = \Delta H_v - RT \tag{2-80}$$

where ΔH_v is the molar enthalpy of vaporization at temperature T. Solubility parameters at 25 °C may range from low values such as 6 $(cal/cm^3)^{1/2}$ for neopentane, to high values such as 23.45 $(cal/cm^3)^{1/2}$ for water. Hildebrand and Scatchard developed the concept of regular solutions, which for binary mixtures of noninteracting, nonpolar molecules predicts that the activity coefficient can be given by using only pure component data (Reid et al. 1977)

$$RT \ln \gamma_1 = V_1^2 z_2^2 (\delta_1 - \delta_2)^2 \tag{2-81}$$

$$RT \ln \gamma_2 = V_2^2 z_1^2 (\delta_1 - \delta_2)^2 \tag{2-82}$$

where z_i is the volume fraction of the component in the binary mixtures. For many systems, an interaction energy density term W $[(cal/cm^3)^{1/2}]$ must be introduced into Equations 2-81 and 2-82. This term is essentially an empirical parameter which is difficult to predict owing to lack of understanding of intermolecular forces (Campbell et al. 1983; Reid et al. 1977). The regular solution theory may be extended to mixtures containing polar components by dividing the solubility parameter into separate contributions from nonpolar (dispersion) forces and polar forces. This approach also requires the use of an empirical correction term (Campbell et al. 1983; Weimer and Prausnitz, 1965). The activity coefficient for solid solutes can also be estimated using regular solution theory with empirical constants and molar volume of the subcooled liquid and solubility parameter of the subcooled liquid. Procedures for estimating these two parameters are described by Prausnitz (1969). Weast (1983) and Barton (1983) tabulate solubility parameters for various organic compounds, both liquid and solid, at 25°C.

The log-linear solubility relationship (Equation 2-78) is related to the Hildebrand solubility theory. The activity of a solute (subscript 2) in a binary solvent mixture (subscript 1) is given as

$$\log \gamma_2 = \left(\frac{V_2 z_1^2}{2.3RT}\right)(\delta_1^2 + \delta_2^2 - 2W) \tag{2-83}$$

$$= A\,(\delta_1^2 + \delta_2^2 - 2W) \quad \text{where} \quad A = \frac{V_2 z_1^2}{2.3RT} \tag{2-84}$$

where δ_1^2 is a volume fraction average of the solubility parameters of the components in the binary solvent mixture, W is the interaction energy density of solute and solvent, V_2 is the solute molar volume, and z is the total volume fraction of the two solvents in the solution (Martin et al. 1982). The relationship between solute activity and mole fraction solubility in pure water, γ_w and X_w respectively, and that in a water/co-solvent mixture, γ_2 and X_2 respectively is

$$\log \gamma_2 + \log X_2 = \log X_w + \log \gamma_w \tag{2-85}$$

This equation may be combined with Equations 2-83 or 2-84 and expressed as a power series in terms of co-solvent volume fraction, z,

$$\frac{\log \gamma_2}{A} = -C_o + C_1 z - C_2 z^2 + C_2 z^3 - \text{----} - (-1)^n C_n z^n \tag{2-86}$$

Regression analysis of experimental data can be used to obtain the coefficients C_o, C_1, C_2, -- etc. Equation 2-86 can be combined with Equation 2-85 to give a form of an extended Hildebrand solubility expression

$$\log X_2 = \log X_w + \log \gamma_w - C_oA + C_1Az - C_2Az^2 + \text{----} \tag{2-87}$$

Martin et al. (1982) showed that the solubility of semi-polar drugs in co-solvent/water systems could be described by Equation 2-87 as a fourth degree power series, as well as by a simplified expression

$$\log X_2 = \log X_w + (\log \gamma_w - C_oA) + C_1Az \tag{2-88}$$

Further, it was noted by Martin et al. (1982) that if regression analysis of Equation 2-88 was performed with perfect accuracy, then log γ_w would be equal to C_0A in order that $X_2 = X_w$ as $z \rightarrow 0$. Hence, with the quantity in parenthesis of Equation 2-88 being numerically small, it may be neglected and

$$\log X_2 = \log X_w + C_1Az = \log X_w + \sigma z \qquad (2\text{-}89)$$

This is a log-linear solubility relationship expressed in terms of mole fraction solute solubility and volume fraction co-solvent. In tests with caffeine in dioxane-water mixtures at 25°C, it was found by Martin et al. (1982) that Equation 2-89 was applicable over a certain range of solvent composition. It was observed that caffeine increased in solubility to a maximum at about 70% volume fraction dioxane, and then decreased over the range 70% to 100% dioxane (Martin et al. 1982). Thus, the log-linear solubility relationship appeared to apply only over part of the solubility curve (0 ~ 30% of dioxane). This was explained by the solubility parameter for caffeine (δ=13.8) being between that for dioxane (δ=10.01) and water (δ=23.45). According to regular solution theory, the solubility of a compound is maximum at solvent composition where the solubility parameter for the solvent mixture is equal to that for the solute. This was evident for caffeine as solubility increased and then decreased in response to change in volume fraction weighted average solubility parameters of the solvent mixture. It was concluded that a log-linear solubility relationship should not be anticipated for solutes having solubility parameters between that for the two co-solvents, and that the log-linear relationship applies particularly well where the solubility parameter of the solute is three or four units smaller than that of the organic co-solvent in water/co-solvent mixtures. This has been observed for example with ethyl p-aminobenzoate (δ=12) in propylene glycol (δ=14.99) and water (δ=23.45) mixtures, where the solubility of ethyl p-aminobenzoate increases logarithmically with increase in volume fraction of propylene glycol. Martin et al. (1982) and Lindstrom (1979) tested the log-linear model for predicting the solubility of methylparaben (δ=11) in aqueous solutions containing various concentrations of ether, formamide, methyformamide or dimethylformamide (δ=12.14). It was found that methylparaben solubility in the mixed solvent systems could be expressed by the log-linear relationship approach only up to z = 0.5 owing to the limitations of the log linear model.

In addition to water/co-solvent systems, Martin et al. (1982b) investigated systems consisting of nonpolar co-solvent mixtures having solubility parameters lower than the solubility parameters of the solute. The systems studied were solubility of testosterone (δ=10.9) and testosterone propionate (δ=9.5) in cyclohexane (δ=8.2) with co-solvents such as chloroform (δ=9.1), ethyloleate (δ=8.6) and isopropyl myristate (δ=8.9). It was found that the log-linear relationship could not be applied to these systems. A system of benzoic acid (δ=11.5) in various proportions of hexane (δ=7.3) and ethyl acetate (δ=8.9) had been investigated by Chertkoff and Martin (1960). A plot of log solubility of benzoic acid versus volume fraction of ethyl acetate co-solvent was attempted, and it was found that the plot showed considerable curvature. The plot was fitted by a quadratic equation of the extended Hildebrand solubility approach (Chertkoff and Martin, 1960).

It is concluded that the log-linear solubility relationship describes systems of semi-polar solutes with water/co-solvent mixtures when the solubility parameters of the solute is about 3 solubility parameter units lower than that of the co-solvent in the water/co-solvent mixture. When the co-solvent is a strong solvating agent, the solute solubility may be described by the log-linear relationship up to 100% co-solvent even though the solubility parameters of solute and solvents are similar. For example a sulfadiazine-dimethylformamide-water system displayed this behavior (Martin et al. 1982). However, for systems where the solute solubility parameter is between the solubility parameters of water and co-solvent, and for systems with solute solubility parameters higher than both of the solvents, the log-linear solubility relationship may be applied only over a limited range of solvent mixtures.

Molecular Surface Area Approach

Yalkowsky et al. (1976) evaluated the increase in aqueous solubility of nonpolar drugs upon addition of a co-solvent. These authors surveyed the pharmaceutical literature and concluded that an exponential increase in solubility was observed for many classes of drugs as long as the solute was less polar than the mixed solvent. A molecular and group surface area approach was developed to describe this phenomena. This approach is based on correlating the mole fraction solubility of a liquid solute in a water/co-solvent mixture to the solute hydrophobic surface area (HSA) and polar surface area (PSA). The total surface area (TSA) of the solute is equal to the surface area of the polar moiety (PSA) plus the hydrocarbonaceous surface area (HSA)

$$\mathrm{TSA} = \mathrm{PSA} + \mathrm{HSA} \qquad (2\text{-}90)$$

and the solute solubility in a solvent/water mixture can be expressed as

$$\ln X_{2,m} = \ln X_{2,3} + z_1 \left[\frac{\Delta\epsilon_H\,(\mathrm{HSA}) + \Delta\epsilon_p\,(\mathrm{PSA})}{kT}\right] \qquad (2\text{-}91)$$

where $X_{2,m}$ is the mole fraction solute solubility in water/co-solvent mixture, $X_{2,3}$ is the mole fraction solute solubility in water, z_1 is the solute-free volume fraction of co-solvent, k is the Boltzman constant, T is the system temperature, $\Delta\epsilon_H$ describes the microscopic interfacial free energy between hydrocarbonaceous surface area and the solvent, and $\Delta\epsilon_p$ is an analogous interfacial free energy term which is dependent upon the interaction between the solvent and the polar portion of the solute. For the case of relatively nonpolar compounds, the hydrophobic interactions are dominant relative to polar interactions. This is equivalent to assuming that the term $\Delta\epsilon_H$ HSA is much greater than the term $\Delta\epsilon_p$ PSA. Under these conditions Equation 2-91 can be reduced to

$$\ln X_{2,m} = \ln X_{2,3} + z_1 \frac{\Delta \epsilon_H \text{ (HSA)}}{kT} \qquad (2\text{-}92)$$

The molecular surface area model shows that in pure co-solvent, the solute mole fraction solubility, $X_{2,1}$, increases exponentially with increase of hydrocarbonaceous surface area of the solute. The molecular surface area model also shows that in binary solvent mixtures, the solute mole fraction solubility increases log-linearly as the fraction of co-solvent, z_1, increases. Yalkowsky et al. (1976) found the mole fraction activity coefficient of alkyl p-aminobenzoates decreased with increase of molecular surface area in pure solvents and in propylene glycol-water mixtures, and that the solubilities of five alkyl p-aminobenzoates gave a linear increase in log mole fraction solubility. It was also found that mole fraction solubility of hexyl p-aminobenzoate in six solvent-water systems increased log-linearly with increase of volume fraction of co-solvent.

Although the molecular surface area approach shows good agreement with published experimental results and appears attractive, it is limited in application by lack of information for values of microscopic interfacial energies, i.e. $\Delta \epsilon_H$ and $\Delta \epsilon_P$. These data are experimentally determined and are available for only a few solvents. This approach is also limited in that the proportion of total surface area attributable to HSA and PSA is generally not known, nor can these parameters be predicted in a straightforward manner. For these reasons, the molecular surface area approach has been judged to be theoretically pleasing but not especially useful in the context of environmental engineering applications; however, this situation may change as a result of experimental programs which are currently in progress under the direction of Professor Yalkowsky (Yalkowsky, 1985).

Intermolecular Forces and Solute Solubility

The previous discussion has explained thermodynamic approaches for estimating solute solubility in mixed solute systems. This chapter concludes with a brief review of the various intermolecular forces that influence solubility of aromatic solutes in water and in organic solvents. The purpose of this discussion is to present the relevant physical and chemical phenomena that influence organic solute solubility in order that some intuition may be gained with respect to qualitative aspects of solubilization. Just as thermodynamic properties of pure substances are determined by intermolecular interactions, so are thermodynamic properties of mixtures dependent upon intermolecular forces which are operative between the molecules of the mixture. These forces include nonspecific dispersive forces, polar interactions, and hydrogen bonding characteristics.

Dispersive Interactions

The intermolecular forces may be divided between chemical forces which extend over very short distances and which entail merging of electron clouds, and electrical-type forces which extend over larger distances. Aside from hydrogen-bonding which is a special case of chemical and electrical-type forces, the general process of solubilization does not entail the formation of chemical bonds, and electrical-type forces are the principal interactions governing this phenomena. Besides electrical forces of attraction that follow Coulomb's law, there are other electrical-type forces including those forces between molecules possessing a permanent dipole and those forces between a molecule which induces a dipole in another molecule. Dispersive, or London-van der Waals forces, arise between atoms or molecules constituting systems of oscillating charges that induce synchronized dipoles that attract each other.

Dispersion forces exist between every pair of adjacent molecules and those interactions normally account for the major part of the interaction energy that holds molecules together in the liquid phase (Prausnitz, 1969). Dispersion forces occur as a result of the fact that the electrons associated with a molecule are in constant random motion and at any instant in time the electrons of the molecule have a specific configuration. This results in an instantaneous dipole moment which can then induce an interactive force in another molecule, and this can result in a net attraction between these two molecules. Dispersive interactions are independent of the interaction of permanent molecular dipoles, and are closely related to the refractive index values of the compound. Dispersive interactions become stronger the greater the refractive index of a compound. In general, refractive index is greater for compounds with unsaturated bonds, and for compounds with elements from the second and third rows of the periodic table. Table 2-1 gives the refractive index and other physical properties of the solutes and solvents used in this investigation. London-van der Waals interactions are in the energy range of 2-10 Kcal/mole.

Dipole Moment

The dipole moment of a molecule may be explained by considering a particle as having two electric charges of the same magnitude, e, but of opposite sign, held a distance l apart. Such a particle has a permanent dipole moment, μ, defined by $\mu = e\ l$. The common unit for dipole moment is the Debye (1 Debye = 10^{-18} esu-cm). The permanent dipole in one particle can then induce a dipole in a second particle, just as may occur with dispersive interactions. The net effect is an increase in the total interaction between these two particles due to the permanent dipole originally present in one of the molecules. The potential energy of interaction between two permanent dipoles i and j is obtained by considering electrostatic forces between the four charges and by averaging over all orientations. Prausnitz (1969) suggests that for a pure polar substance, the potential energy of interaction varies with the fourth power of the dipole moment. Thus a small increase of the dipole moment can produce a large change in the potential

Table 2-1: Physical Properties of Solutes and Solvents*

	Refractive Index [-]	Dielectric Constant $\left[\frac{esu^2sec^2}{g\ cm^3}\right]$	Dipole Moment [Debye]
Solvents			
Water	1.62226	78.54	1.85
Methanol	1.3288	32.63	1.70
Ethanol	1.3611	24.30	1.69
Propanol	1.3850	20.1	1.66
Acetone	1.4535	20.7	2.88
Solutes			
Naphthalene	1.5898	2.54	0
Naphthol	1.6224	NA	NA
Quinoline	1.6261	9.00	2.29
3,5-Dichloroaniline	NA	NA	NA
Aniline	1.600	6.89	1.53
Phenanthrene	1.5943	2.80	0
o-Xylene	1.5055	2.57	0.62

*: Taken from Weast R.C. (1982).

NA: not available.

energy of interaction due to permanent dipole forces. Table 2-1 shows values of the dipole moment for the solutes and solvents used in this study.

Dipole interactions are quite short range, and this allows for dipole interactions to be determined by the sum of functional group dipoles within a molecule (Snyder, 1978). For example, in aromatic compounds with para-isomers of the same substituent, the overall dipole moment of the para-compound is zero because of cancellation of group dipole effects, while group dipoles are additive in ortho-isomers. Nonetheless, the dipole interactions of ortho- or para- isomers with surrounding molecules are in fact quite similar, because two polar groups exist in each molecule, and the individual polar groups can undergo dipole interactions (Snyder, 1978). For these reasons, dipole interactions often play an important role in affecting compound solubility and separation.

Hydrogen bonding

The most common chemical effect encountered in solution thermodynamics is that due to the hydrogen bonding, H-bonding (Prausnitz, 1969). While the "normal" valence of hydrogen is unity, many hydrogen bond-containing compounds behave as if hydrogen were bivalent. Hydrogen bonding is an interaction between a "covalently" bonded H atom (A-H) having the tendency to be donated, and a region of high electron density on an electronegative atom or group of atoms, B, which can accept the H atom. Typical proton donor groups include hydrogen bonded covalently to electronegative atoms such as O, N, S, halogens and in special cases, carbon. Table 2-2 classifies H-bonds into four types (A, B, AB and N) in which H-bond refers to an interaction according to the operational criteria of Pimentel and McClellan (1960). The H-bond leads to the formation of molecular aggregates, which in many aspects conform to the criteria of chemical bond. However, H-bonds differ from chemical bonds in that H-bonds exist in a state of dynamic equilibrium. This is evident by comparison of differences in bonding strengths. The bonding strength for ordinary chemical bonds is on

Table 2-2: Classification of Compounds by Hydrogen Bonding*

Compound Class	Molecule Contains: Proton Donor (Acid)	Molecule Contains: Proton Acceptor (Base)	Examples
A	Yes	No	Haloforms, highly halogenated compounds, acetylenes
B	No	Yes	Ketones, aldehydes, ethers, tertiary amines, olefins, aromatics, nitriles
AB	Yes	Yes	Water, alcohols, carboxylic acids, phenol, primary and secondary amines
N	No	No	Saturated hydrocarbons, carbon disulfide, carbon tetrachloride

* After Pimentel and McClellan (1960)

the order of 50 to 200 Kcal/mole, while that for H-bonds is on the order of 2 to 10 Kcal/mole.

An unassociated substance which contains an H-bond group (type-A or type-B) is usually more soluble in a solvent that can supply the other partner in an H-bonding interaction. There are many examples, such as solubilization of chloroform or acetylene (type-A) in ethyl ether or acetone (type-B) (Pimentel and McClellan, 1960). In these mixtures, there is strong H-bonding between the proton donor and proton acceptor group. Type-A or -B compounds are usually soluble in type-AB compounds, although this depends on the strength of the electron donor and acceptor group of the type-A and -B molecules, and preexisting H-bonding in the type-AB molecule. The solubility of type-AB compounds is complicated by these compounds being able to self associate to form dimers or trimers, or to form H-bonds within a single molecule. The self-associating tendency of type-AB molecules may be disrupted when those molecules are mixed with a strong donor or acceptor molecule.

Hydrophobic Effects and Polarity

Hydrophobic compounds are viewed as substances that are readily soluble in many non-polar solvents but only sparingly soluble in water. These substances are considered distinct from substances that have generally low solubility in all solvents owing to the formation of solids with strong intermolecular cohesion (Tanford, 1973). Hydrophobic effects are said to be associated with non-polar solutes in polar solvents, in which the non-polar group plays a minor role compared to the attractive forces between water molecules. Water "squeezes" out the hydrophobic solute molecules because the interaction of hydrophobic solute and water are much weaker than the interaction between water molecules. The hydrophobic effect is less pronounced for cyclic aromatic hydrocarbons than for saturated cyclic hydrocarbons because the electrons in the aromatic compound lead to stronger van der Waals attraction to water molecules (Tanford, 1973). The aliphatic alcohols are relatively good solvents for hydrocarbons, because the local molecular organization segregates the hydrocarbon tails from the OH group such that no major reorganization is required to accommodate hydrocarbon molecules.

The concept of polarity has been employed in a somewhat analogous manner as hydrophobicity to describe solubilization phenomena. Rohrschneider (1966) has used polarity as a principal means to describe solvent characteristics, much as solubility parameter is used in regular solution theory. Rohrschneider's description of overall solvent polarity is expressed as an E_T value in units of Kcal/mole. This value attempts description of dipole interactions and proton donor/acceptor interactions. It is obtained through experiments with model solutes, each of which exemplifies a particular solute-solvent interaction. Solvent E_T values reported for compounds of interest in this investigation are shown in Table 2-3. These values are examined later during qualitative evaluation of the experimental solubility data.

Solubility Parameters

Dispersive interactions between nonelectrolytes may be understood in consideration of the solubility parameter concept developed by Hildebrand (Hildebrand, 1970). This concept was discussed briefly under log-linear solubility relationships. The concept helps to quantify an old rule: "like dissolve like." This rule refers to various solubility observations such as an aromatic hydrocarbon like naphthalene dissolving better in aromatic solvents such as benzene and toluene than in aliphatic solvents such as hexane, and hardly dissolving at all in water. In this rule, "like" may be characterized by the solubility parameters for solute and solvent. The solubility parameter is defined as the square root of the cohesive energy density, C, as given by Equation 2-79. The values of solubility parameters for the solutes and solvents used in this study are tabulated in Table 2-4.

Table 2-3: Solvent Polarity Using E_T as the Indicator

Solvent	Solvent Polarity E_T [Kcal/mole]
Water	63.1
Methanol	55.5
Ethanol	51.9
Propanol	50.7
Acetone	42.2
Aniline	44.4
Quinoline	39.4

Reference: Dimroth and Reichardt (1966).

For binary mixtures of noninteracting, nonpolar molecules the solubility parameter concept predicts that the activity coefficient can be given from pure component data (Reid et al. 1977). If the fugacity of the solute (denoted by subscript 2) in the pure liquid state is represented by f_2° and the fugacity of the solute in the solution by f_2, then, the solubility of the solute can be evaluated by

$$RT \ln \frac{f_2}{f_2^\circ} = RT \ln a_2 = -RT \ln X_2 + V_2 z_1^2 (\delta_1 - \delta_2)^2 \qquad (2\text{-}93)$$

where a_2 is the activity of the solute, X_2 is the solute mole fraction solubility, and z is the solvent volume fraction in the mixture. The solubility parameter theory predicts that the solubility of a solute in a solvent will increase as the absolute difference, $\Delta\delta$, between solubility parameter for the solute and the solvent decreases. Thus one predicts for the case of five solvents shown in Table 2-4 that the solubility of naphthalene would be highest in acetone followed by propanol, ethanol, methanol, and water. The Hildebrand theory predicts that the solubility parameter of a mixture is the weighted arithmetic mean of the solubility parameters of the constituent pure solvents (Hildebrand and Scott, 1970). Thus, the solubility parameter, δ_{13}, of a mixture of solvents 1 and 3 is

$$\delta_{13} = \delta_1 z_1 + \delta_3 z_3 \qquad (2\text{-}94)$$

where z_1, z_3 are the volume fraction of solvents 1 and 3 in the mixture, and δ_1 and δ_3 are the solubility parameters of pure solvents 1 and 3 respectively.

Solubility parameter concepts can be used to interpret relationships involving: liquid miscibility, polymer solubility, polymer compatibility, dispersion phenomena, solubility of inorganic compounds, and organic material in organic solvents (Hansen, 1969; Tijssen et al. 1976, Freeman and Cheung, 1982). However, it must be recognized that the solubility parameter concept was developed on the basis that non-specific dispersion forces are

Table 2-4: Solubility Parameters of Solvents and Solutes

Compound	δ	δ_d	δ_p	δ_H	δ_a	δ_b
Solvent						
Water	23.50	7.22	15.35	19.07	16.65	10.9
Methanol	15.15	7.18	6.70	13.53	7.18	12.9
Ethanol	13.09	7.46	4.29	10.81	5.17	11.3
Propanol	11.78	7.65	5.54	9.04	4.12	10.0
Acetone	9.93	7.44	6.41	5.47	0.90	16.6
Solute:						
Naphthalene	9.9	9.9	9.4	1.0		
Naphthol	10.2					
Quinoline	10.8					
3,5-Dichloroaniline	NA					
Aniline	11.81	9.04	2.30	7.88	3.49	8.9
Phenanthrene	9.8					
o-Xylene	8.8	8.65	8.5	0.5		

δ = Solubility parameter (overall)
δ_d = Solubility parameter due to dispersive force
δ_p = Solubility parameter due to dipole induction
δ_H = Solubility parameter due to hydrogen bonding
δ_a = Solubility parameter due to proton donor ability
δ_b = Solubility parameter due to proton acceptor ability

Reference: Snyder, (1979).

normally the dominant solution interaction forces. Consequently, the solubility parameter theory does not work as well for strongly polar solvents and solutes. Furthermore, the solubility parameter theory assumes symmetrical interactions between adjacent molecules in solution, which for example, does not occur during H-bonding.

More recent work has led to a broader interpretation of the original Hildebrand solubility parameter approach. An alternative approach is based on a combination of the original Hildebrand solubility parameter theory plus an experimentally based solvent classification scheme (Karger et al. 1978, Snyder, 1980, Hansen, 1967). This alternate approach separates the interaction between solvent and solute molecules into partial solubility parameters: dispersive, δ_d; dipole, δ_p; and H-bonding, δ_H, δ_a, δ_b. Partial solubility parameters are assigned to account for these specific interactions, and these individual solubility parameters provide a better measure of how a given solvent will interact with a particular solute. The maximum solubility occurs when the partial solubility parameters of solvent and solute are matched. In this approach, hydrogen bonding interactions can be divided into partial solubility parameters as indicated by δ_a (for acid or proton donor) and δ_b (for base or proton acceptor). Maximum solubility occurs when the product of δ_a for the solvent and δ_b for the solute (or vice versa) is a maximum, rather than when these values are equal for both solvent and solute. That is, maximum solubility is promoted by strong hydrogen bonding between solvent and solute molecules. For a solvent with a high value of δ_a and low value of δ_b, hydrogen bonding with a solute will be strongest when the solute has a large value of δ_b, rather than when the solute is also a strong donor and weak acceptor. Table 2-5 describes several features of the partial solubility parameters and the related solvency characteristics.

The partial solubility parameter approach allows for quantitative prediction of solvency for different polar solvent-solute combinations. However, extended solubility parameter treatment as based on partial solubility parameters still has some limitations (Snyder, 1980):

Table 2-5: Partial Solubility Parameters*

Partial Solubility Parameter	Related to	Maximum Solvency
δ_d	Polarizability or refractive index	Equal values of δ_d for solute and solvent
δ_p	Dipole moment of groups within solvent and solute molecule	Equal values of δ_p for both solvent and solute
δ_H	Hydrogen bonding	Maximum value of $[(\delta_a)_{solute}(\delta_b)_{solvent}]$ or $[(\delta_a)_{solvent}(\delta_b)_{solute}]$
δ_a	Acidity or proton-donor strength in hydrogen bonding	Minimum value of $[(\delta_a)_{solute}(\delta_b)_{solvent}]$ or $[(\delta_a)_{solvent}(\delta_b)_{solute}]$
δ_b	Basicity or proton-acceptor strength in hydrogen bonding	

[*] From Snyder (1978)

- One must know the composition of the sample to be dissolved.
- It requires partial solubility parameter values for solutes as well as for solvents, and generally solute solubility parameters are not available.
- The resulting equations for relative solubility are rather complicated, which discourage their use.
- There is a tendency to underestimate δ values for strong proton accepting solvents.
- Solvents which comprise alcohol or water give poor agreement due to strong self-association, and thus there is deviation from regular solution behavior.

Thus, the expanded solubility parameter approach is still limited by some of the other assumptions in the original Hildebrand theory. Barton (1983) provides a compilation of empirically derived partial solubility parameters for use in polymer chemistry and chromatography, and for estimating various interactions in the liquid state.

Summary

This chapter has provided a synthesis of information on chemical thermodynamic techniques that may describe the solubility of nonelectrolytes in solution. The information presented in this chapter was employed to assess several theoretical approaches which may be used to predict organic solute solubility in water/co-solvent mixtures. The next chapter describes results of experimental studies to observe aromatic solute solubility in water/co-solvent systems. These data are then used with other observations to evaluate the predictive methodologies.

Chapter 3

EXPERIMENTAL MEASUREMENT OF SOLUTE SOLUBILITY IN SOLVENT/WATER MIXTURES

Introduction

The experimental portion of this part of the investigation entailed measurement of solubility for four aromatic hydrocarbons. Aromatic solute solubilities were measured in aqueous solution with and without addition of organic co-solvent. The organic co-solvents which were evaluated were methanol and acetone. The analytical technique employed was high pressure liquid chromatography (HPLC) for the analysis of aromatic solutes in water and in water/co-solvent systems. The results of this experimentation are discussed in the following chapter in which an evaluation of the co-solvent effect on solute solubility is presented. That presentation is then followed by a discussion of results of experiments to evaluate the effect of co-solvent on solute adsorption onto soil.

Experimental Components

Materials

The solutes used in this study were selected in order to represent important types of aromatic hydrocarbons having different hydrogen bonding characteristics. Naphthalene ($C_{10}H_8$) was selected as the principal solute for this investigation because it is the "building block" for polycyclic aromatic hydrocarbons. Naphthalene is classified as a N-type compound with respect to hydrogen bonding characteristics, which means it does not form hydrogen bonds with hydrogen donors (A- or AB-type compounds) or hydrogen acceptors (B- or AB-type compounds). Two derivatives of naphthalene were also investigated, α-naphthol ($C_{10}H_7OH$) and quinoline (C_9H_7N). α-Naphthol is referred to in the following as "naphthol", and this compound is classified as an AB-type compound while quinoline is classified as a B-type compound with respect to hydrogen bonding characteristics. Thus naphthol may hydrogen bond with AB- or B-type solvents while quinoline may hydrogen bond with A- or AB-type solvents. A chlorinated aromatic hydrocarbon, 3,5-dichloroaniline ($C_6H_3NH_2Cl_2$), was also investigated in this study. This solute was selected because it has some of the functional group characteristics of degradation products of certain pesticides. These solutes were obtained from Fisher Scientific Company (Pittsburgh, PA) or Aldrich Chemical Company (Milwaukee, WI). Scintillation grade naphthalene, and certified A.C.S. grade naphthol, quinoline and 3,5-dichloroaniline having purity of 98% or higher, were used in the study. The solutes were used in this study as received without further purification.

The polar solvents used in this study were methanol (CH_3OH) and acetone (CH_3COCH_3). Methanol is classified as an AB-type of solvent and acetone is a B-type solvent in terms of the hydrogen bonding interactions. Methanol and acetone were selected because of differences in their physical/chemical properties and because these solvents are major organic solvents of commerce. Other solvents used in this study were methylene chloride (CH_2Cl_2) for glassware cleaning, and acetonitrile (CH_3CN) for HPLC analysis. These solvents were HPLC grade as obtained from Fisher Scientific Company (Pittsburgh, PA). The solvents have greater than 99.9% purity and were used in this study as received.

Water used in these experiments was organic-free and deionized. The water was prepared by passing tap water through a system consisting of a filter, resin ion exchange column and carbon column. This equipment was supplied from Continental Water (El Paso, TX). Organic solvents and water were filtered through 0.45 μm filters (teflon and cellulose, respectively), degassed by a vacuum and purged with helium prior to use in HPLC analysis.

Glassware

All glassware used in this investigation was carefully cleaned in order to minimize interferences. Glassware was first cleaned with detergent and water, and then rinsed with deionized water. After this general cleaning procedure, the glassware was soaked in a 1:1 nitric acid bath for 24 hours and then rinsed successively with deionized water, methanol, acetone and methylene chloride. Following these cleaning procedures, the glassware was oven dried at 105°C; the glassware was then covered with aluminum foil prior to use. Solubility and adsorption measurements were performed with use of 50 ml screw top glass centrifuge tubes. These tubes were sealed with a teflon-lined septum which was held in place by means of a screw cap having an access hole. This permitted the withdrawal of a sample for analysis by insertion of a microliter syringe through the septum.

Experimental Instruments

Solute solubility determinations were accomplished by high pressure liquid chromatography (HPLC) techniques. A Perkin-Elmer (Norwalk, Conn.) Series 3 reverse phase high pressure liquid chromatography system was used in this investigation. The HPLC was operated by using a constant flow gradient pumping system with acetonitrile and water, and a reverse phase column. The acetonitrile and water were used as carrier solvents, and these solvents were proportionally mixed with the aid of two calibrated HPLC pumps. Detection was accomplished by either a Perkin-Elmer model LC-15 ultraviolet (UV) detector equipped with a 254 nm filter, or by a Perkin-Elmer model 204-S fluorescence detector which provided variable excitation and emission wavelength settings. Samples were injected using a Rheodyne (Berkeley, CA) Model 7105 injection valve fitted with a 175 μl sample loop. Injected sample volume ranged between 2 and 8 microliters. Samples were withdrawn from the centrifuge tube by a Hamilton (Reno, Nevada) 800 series microliter syringe and injected directly for HPLC analysis.

A Perkin-Elmer 2.6 mm x 25 cm PAH/10 column and a Supelco (Bellefonte, PA) 4.6 mm x 25 cm LC-PAH column were used to provide resolution of naphthalene and naphthol. The absorbance was then quantified by using the fluorescence detector. For naphthalene analysis, the fluorescence detector showed the best resolution at an excitation wavelength of 280 nm and an emission wavelength of 340 nm, while for naphthol the fluorescence detector showed the best results at an excitation wavelength of 310 nm and an emission wavelength of 340 nm. Details of programs used in HPLC analysis are described in Table 3-1.

A Supelco 4.6 mm x 15 cm (5 μm packing) LC-8 column was used to provide resolution of quinoline and 3,5-dichloroaniline. A fixed-wavelength (254 nm) UV detector was used for quantification purposes. Table 3-1 shows the parameters used in the HPLC analysis for quinoline and 3,5-dichloroaniline.

Experimental Procedures to Measure Solute Solubility

The solubility of aromatic solutes in pure solvent (i.e. water, methanol and acetone) and binary solvent mixtures (i.e. methanol/water, and acetone/water) were determined by batch tests with a solution phase comprised of 0.01 N calcium chloride. The calcium chloride was used to maintain a background electrolyte concentration, and in this respect the experimental protocol was consistent with the subsequent sorption tests described in Chapter 5 in which calcium chloride was used to improve soil particle coagulation and settling after attaining sorption equilibrium. The amount of calcium chloride added to the samples maintained 0.01 equivalents of $CaCl_2$ per liter of solution, regardless of the volume fraction of solvent. This represents a relatively small amount of electrolyte, and thus it should have no effect on solute solubility owing to "salting out" effects.

The organic solutes, particularly naphthalene, were volatile to some degree at room temperature. Therefore, in order to eliminate volatilization loss, all tests were conducted in sealed 50 ml glass centrifuge tubes

Table 3-1: Specifications for HPLC Analysis

	*Naphthalene	Naphthol	Quinoline	3,5-Dichloroaniline
Column	PAH/10* LC-PAH**	PAH/10* LC-PAH**	LC-8**	LC-8**
Detector	fluorescene	fluorescene	UV	UV
Flow rate [ml/min]	1.0	1.0	2.0	2.0
Acetonitrile [% vol.]	60%	55%	40%	50%
Excitation wavelength (nm)	280	310	-	-
Emission wavelength (nm)	340	340	-	-
UV wavelength (nm)	-	-	254	254
UV aufs	-	-	0.128	0.128
Retention time (min)	7.8	4.7	4.3	2.7

* HPLC column obtained from Perkin-Elmer Corp.

** HPLC column obtained from Supelco Co.

equipped with a screw-top and teflon liner septum. Solubility experiments were performed by placing excess solute in the centrifuge tube and filling with deionized water containing the electrolyte and co-solvent. The water or co-solvent/water mixture was added to fill the centrifuge tubes in a manner to leave no head space, then the centrifuge tubes were sealed with the teflon-lined septum and transferred to a wrist-action shaker (Model 74, Burrell Corp., Pittsburgh, PA). Centrifuge tubes were covered with aluminum foil in order to eliminate photodegradation. These centrifuge tubes were then shaken at room temperature (23 ± 2°C) for 24 hours to allow equilibrium to be achieved. The samples were then centrifuged for 1 hour at 8000 rpm using a IEC clinical centrifuge (International Equipment Co. Needham, MA), after which 2 to 8 microliters of sample solution were withdrawn from the centrifuge tubes and injected directly with the microliter syringe for HPLC analysis. The septum port allowed for samples to be withdrawn without the possibility for loss of solute by volatilization.

Each experimental setup was run in duplicate, and then the experiment was repeated. Thus each test was performed in quadriplicate. This allowed for sample-by-sample comparison to ensure correctness of procedure and validity of the results. Each sample was analyzed by performing at least two, and usually three, injection determinations. Therefore the number of determinations exceeded the number of samples analyzed by a factor of two to three. Analytical standards were measured at the beginning of each series of analyses. Standards were also measured following every three samples in order to ensure reproducibility in instrument response factors.

Screening tests were performed to ensure that aqueous phase equilibrium was achieved within 24 hours. These tests were performed with naphthalene, the least soluble solute employed in experiments in this investigation, and methanol volume fractions of 0.0, 0.05, 0.1 and 0.5. The duration of these tests ranged from 24 to 120 hours, and the results showed no increase in solute solubility beyond that attained after twenty-four hours of equilibration.

Experimental Results

Solute solubility was evaluated at least three times for every combination of solute and water/co-solvent. For the case of naphthalene and methanol/water mixtures, there were 108 individual samples comprising 12 different solvent volume fractions (0, 0.005, 0.01, 0.05, 0.1, 0.5, 1, 5, 10, 20, 30, 40, 50, and 100%). These results are shown in Table 3-2. Table 3-3 shows the results of measurement of naphthalene solubility in acetone/water mixtures, for which 48 samples were evaluated. Table 3-4 presents the results of analysis of 50 samples to measure naphthol solubility in methanol/water mixtures, and Table 3-5 shows the results of analysis of 57 samples to measure naphthol solubility in acetone/water mixtures. Table 3-6 shows the results of analysis of 40 samples to measure quinoline solubility in methanol/water mixtures, and Table 3-7 shows the results of analysis of 48 samples to measure quinoline solubility in acetone/water mixtures. Table 3-8 shows the results of analysis of 51 samples to measure 3,5-dichloroaniline solubility in methanol/water mixtures, and Table 3-9 shows results of 52 samples that were analyzed for 3,5-dichloroaniline solubility in acetone/water mixtures.

Tables 3-2 to 3-9 show the number of samples investigated, the number of individual determinations performed, the average solute solubility, and the standard deviation for each solvent/water combination. The coefficient of variation for the various results shown in Tables 3-2 through 3-9, expressed as standard deviation divided by the average value, ranged from approximately 2% to 15%.

In solvent/water mixtures containing greater than 50% co-solvent by volume, the solubility for most solutes was above the instrument detection limit. Solute solubility measurement for these samples with greater than 50% co-solvent was not attempted because it was believed that additional error would be introduced as a result of sample transfer and dilution. As discussed in Chapter 4, the experimental data for solubility in 100% water, as well as naphthalene solubility in pure methanol agrees with literature values.

Table 3-2: Naphthalene Solubility in Methanol/Water Mixtures

Methanol [% vol.]	Number of Determinations [#]	Average Solubility [mg/l]	Standard Deviation [mg/l]
0	50	30.6	2.65
0.05	19	31.3	1.74
0.1	18	35.1	1.23
0.5	51	38.8	3.18
1	21	39.1	2.16
5	20	46.5	3.55
10	28	58.3	4.95
20	11	104	3.07
30	11	243	19.4
40	11	468	62.9
50	39	1220	189.
100	13	66200	3080.

Total Samples Evaluated: 108

Table 3-3: Naphthalene Solubility in Acetone/Water Mixtures

Acetone [% vol.]	Number of Determinations [#]	Average Solubility [mg/l]	Standard Deviation [mg/l]
0	50	30.6	2.65
5	9	71.0	2.04
10	10	111.	2.66
20	10	417.	10.8
30	10	1080.	112
40	10	3540	155
50	10	10200	832

Total Samples Evaluated: 48

Table 3-4: Naphthol Solubility in Methanol/Water Mixtures

Methanol [% vol.]	Number of Determinations [#]	Average Solubility [mg/l]	Standard Deviation [mg/l]
0	24	846	121
0.1	7	938	124
0.5	9	1020	187
1	8	1170	133
5	12	1210	128
10	24	1310	199
20	14	2020	382
30	12	2850	343
40	17	7160	739
50	16	24300	3120

Total Samples Evaluated: 50

Table 3-5: Naphthol Solubility in Acetone/Water Mixtures

Acetone [% vol.]	Number of Determinations [#]	Average Solubility [mg/l]	Standard Deviation [mg/l]
0	24	846	121
1	8	1210	63.8
5	15	2160	120
10	24	2110	314
20	22	3650	858
30	24	6420	1260
40	16	14900	1570
50	26	28600	3950

Total Samples Evaluated: 57

Table 3-6: Quinoline Solubility in Methanol/Water Mixtures

Acetone [% vol.]	Number of Determinations [#]	Average Solubility [mg/l]	Standard Deviation [mg/l]
0	33	6840	236
1	12	7810	299
5	15	9150	1030
10	15	9880	945
20	16	14800	932
30	15	27400	2060
40	15	71200	3210
50	15	106000	6120

Total Samples Evaluated: 40

Table 3-7: Quinoline Solubility in Acetone/Water Mixtures

Acetone [% vol.]	Number of Determinations [#]	Average Solubility [mg/l]	Standard Deviation [mg/l]
0	33	6840	236
0.5	8	6840	291
1	14	8490	342
5	14	9840	328
10	20	14600	573
20	16	34100	1230
30	12	75900	6900
40	11	127000	20200
50	12	251000	34500

Total Samples Evaluated: 48

Table 3-8: 3,5-Dichloroaniline Solubility in Methanol/Water Mixtures

Acetone [% vol.]	Number of Determinations [#]	Average Solubility [mg/l]	Standard Deviation [mg/l]
0	40	784	33.5
5	16	1030	15.4
10	21	1090	75.2
20	18	1830	277
30	17	3440	221
40	17	7680	249
50	16	19200	1930

Total Samples Evaluated: 51

Table 3-9: 3,5-Dichloroaniline Solubility in Acetone/Water Mixtures

Acetone [% vol.]	Number of Determinations [#]	Average Solubility [mg/l]	Standard Deviation [mg/l]
0	40	784	33.5
1	10	837	37.7
5	14	1100	73.2
10	20	1540	117
20	17	2180	163
30	18	3990	315
40	12	10600	1270
50	12	24000	1250

Total Samples Evaluated: 52

Interferences

Considerations for possible errors associated with this experimental study include losses and/or interferences that may occur at several specific points between sample preparation and analysis. Most of these effects would result in loss of solute. To the extent that this is true, results of the experimental study may become unreliable. Effects which may result in loss of solute include: photodegradation, oxidation, volatilization, adsorption onto an inner surface of glassware, and non-quantitative transfer.

Photodegradation of samples in glassware from exposure to light (e.g. during sample preparation and equilibration) was minimized by covering glassware with aluminum foil and by using amber glassware whenever practical. Losses by oxidation were minimized by: degassing the water and solvent prior to use in making solute solutions, filling the centrifuge tube with solution with no head space, and sealing the centrifuge tube with a teflon-lined septum. Volatile losses were minimized by employing excess solute and by filling the centrifuge tubes with co-solvent/water mixture without any head space, and by maintaining tight seals during the equilibration process. Adsorption on inner surface of the glassware was judged to be inconsequential owing to the fact that the experiments were performed with excess solute being visibly evident in the sample; adsorptive losses were also minimized by avoiding contact of sample solutions with extraneous glassware. Chronic interferences were minimized by carefully cleaning the glassware and periodically cleaning and calibrating the instruments. Errors associated with HPLC analysis relate primarily to uncertainty in measurement of injected volume and peak area calculations. Measurement of injected volume was taken as the difference of syringe sample volume before and after each injection, and peak area was measured on chart recorder paper by use of a planimeter. Standard concentrations of solute were injected after every three samples in order to minimize the instrument response variation.

Chapter 4

PREDICTION OF AROMATIC SOLUTE SOLUBILITY IN SOLVENT/WATER SYSTEMS

Introduction

This chapter evaluates the applicability of the models described in Chapter 2 for estimating solute solubility in binary solvent mixtures. Estimated solute solubilities are compared with experimental solubilities for eight solute-binary solvent systems: naphthalene-methanol/water, naphthalene-acetone/water, naphthol-methanol/water, naphthol-acetone/water, quinoline-methanol/water, quinoline-acetone/water, 3,5-dichloroaniline-methanol/water, and 3,5-dichloroaniline-acetone/water. Experimental solute solubility data were obtained from batch equilibrium tests which were presented in the previous chapter. A limited amount of data for ten additional systems were obtained from the literature, and these systems were also evaluated. These ten systems were: naphthalene-ethanol/water, naphthalene-propanol/water, aniline-methanol/water, aniline-ethanol/water, phenanthrene-methanol/water, phenanthrene-ethanol/water, o-xylene-methanol/water, o-xylene-acetone/water, o-xylene-ethanol/water, and o-xylene-propanol/water. It is evident from the results of this investigation that the available literature on aromatic solute solubility in miscible solvent/water mixtures is not extensive. The data for the ten additional systems evaluated in this study were obtained from Stephen and Stephen (1963), Dean (1973), and Seidell (1941). In addition, Stephen and Stephen (1963) provided some data for naphthalene solubility in methanol/water and acetone/water mixtures. The name "xylene", as used in some figures, refers to the ortho-substituted compound, 1,2-dimethylbenzene, while "naphthol" refers to the compound α-naphthol.

This chapter begins with a discussion of activity coefficient for solutes and solvents in the various co-solvent/water mixtures. The UNIFAC group contribution approach was employed for this task. This discussion is then used with semi-empirical thermodynamic approaches to predict solute solubility in pure solvent. The chapter concludes with an evaluation of the techniques described in Chapter 2 to predict aromatic solute solubility in co-solvent/water mixtures.

Activity Coefficient

The activity coefficients for the components in the mixed solvent systems were estimated by a group contribution method using the UNIFAC approach. The UNIFAC approach computes activity coefficients from knowledge of the molecular structure of the solute and solvents through an equation which contains interaction parameters of the various functional groups. The UNIFAC approach consists of a two-part calculation to obtain the component activity coefficient: a combinatorial part, which is essentially due to difference in size and shape of molecules, and a residual part, which is essentially due to energy of interactions between functional groups. The theoretical framework for the UNIFAC model was described in Chapter 2. The basic steps for estimating activity coefficient are:

1. Draw the molecular structure of every component in the multicomponent system.
2. Determine the functional group type and number of functional groups in each molecule.
3. Calculate r_i and q_i using values of R_k and Q_k
4. Calculate l_i, ϕ_i and θ_i noting that $\Sigma\phi_i=1$ and $\Sigma\,\theta_i=1$
5. Calculate the combinatorial part γ_i^c
6. Calculate ψ_{nm}, Θ_m and X_m
7. Calculate Γ_k and $\Gamma_k^{(i)}$ for each functional group
8. Calculate the residual part γ_i^R
9. Add the combinatorial part, γ_i^c, and the residual part γ_i^R to obtain activity coefficient, γ_i.

A sample calculation is presented in Appendix A to illustrate the computational methodology of the UNIFAC approach. This calculation is performed for prediction of infinite dilution activity coefficient, γ^{∞}, for naphthalene solubility in a system consisting of 50% (by volume) methanol and water. During this investigation, computation of the solute infinite dilution activity coefficients was facilitated by the use of a FORTRAN program which was developed by Fredenslund et al. (1975) and updated by Anderson (1983). Solute infinite dilution activity coefficients in pure solvents were computed using the UNIFAC approach for seven solutes in five pure solvents as shown in Table 4-1. The data presented in Table 4-1 were used to evaluate the aromatic solute solubilities in pure solvents. Calculated infinite dilution activity coefficients for the solutes in eighteen binary solvent systems are presented in Tables 4-2 to 4-4. Table 4-5 shows the activity coefficients for the organic co-solvents and water in the binary solvent mixtures. The activity coefficients presented in Tables 4-2 to 4-5 were calculated in order to show their dependence on solvent volume fraction and to allow estimation of mole fraction solute solubility. The results shown in Tables 4-2 through 4-5 were then used to obtain solute mass concentration (i.e. mg/l or g/l) solubility in systems with different proportions of solvent.

The data in Tables 4-2 to 4-5 show for the aromatic solutes that the activity coefficients decrease with increase of organic solvent content. For example, the activity coefficient for naphthalene in water is 139,000, and this decreases to 1,540 with an aqueous phase containing 50% by volume of methanol. The activity coefficient for naphthalene in 100% methanol is 13, which is 10^4 times less than the activity coefficient in pure water. It is also noted that the activity coefficients for the solutes generally increase with decrease of solute solubility parameter. That is, the activity coefficients for phenanthrene (δ = 8.6), naphthalene (δ = 9.9), quinoline (δ = 10.8), and aniline (δ = 11.8) in water are 7.40×10^6, 1.39×10^5, 1840 and 90.4; and in methanol these values are 2,550, 13.0, 1.80, and 2.46 respectively. This trend is only qualitative at best, as naphthol (δ = 10.2) and o-xylene (δ = 8.8) are out of

Table 4-1: Predicted Infinite Dilution Activity Coefficients for Aromatic Solutes in Pure Solvent Systems

	Water	Methanol	Acetone	Ethanol	Propanol
Naphthalene	139,000	13.0	2.53	14.0	9.30
Naphthol	486	0.79	0.17	NE	NE
Quinoline	1,840	1.80	2.60	NE	NE
3,5-Dichloroaniline	877	0.39	1.77	NE	NE
Aniline	90.4	2.46	NE	1.45	NE
Phenanthrene	7,410,000	25.5	NE	36.9	NE
o-Xylene	56,500	9.59	2.17	6.39	4.52

NE: Not Evaluated

Table 4-2: Predicted Infinite Dilution Activity Coefficients for Aromatic Solutes in Methanol/Water Mixtures

Methanol [% vol.]	Naphthalene	Naphthol	Quinoline	3,5-Dichloroaniline	Aniline	Phenanthrene	o-Xylene
0	139,000	486	1,840	878	90	7,410,000	56,500
10	57,200	239	786	320	40	682,000	10,200
20	23,500	120	347	129	21	97,900	2,590
30	9,590	61	158	55	13	19,300	834
40	3,870	32	74	25	8.5	4,800	322
50	1,540	17	36	12	6.1	1,480	143
70	606	8.7	18	5.5	4.7	525	71
70	235	4.7	9.3	2.7	3.8	213	39
80	90	2.5	5.0	1.3	3.2	96	23
90	34	1.4	2.9	0.7	2.8	48	14
100	13	0.8	1.8	0.4	2.5	25	9.6

Table 4-3: Predicted Infinite Dilution Activity Coefficients for Aromatic Solutes in Acetone/Water Mixtures

Acetone [% vol.]	Naphthalene	Naphthol	Quinoline	3,5-Dichloro-aniline	o-Xylene
0	139,000	486	1,840	878	56,500
10	64,200	34	162	459	6,090
20	28,800	5.6	31	88	1,280
30	12,400	1.5	9.5	23	394
40	5,160	0.52	3.9	8.9	151
50	2,030	0.24	2.0	4.3	67
60	753	0.13	1.2	2.4	32
70	257	0.08	0.91	1.5	16
80	77	0.07	0.83	1.2	8.3
90	18	0.07	1.07	1.1	4.3
100	2.5	0.17	2.60	1.8	2.2

Table 4-4: Predicted Infinite Dilution Activity Coefficients for Aromatic Solutes in Ethanol/Water and Propanol/Water Mixtures

System	Ethanol/Water				Propanol/Water	
Solute	Naphthalene	Aniline	Phenanthrene	o-Xylene	Naphthalene	o-Xylene
Organic Co-solvent [% vol.]						
0	139,000	90	7,410,000	56,500	139,000	56500
10	10,900	15.7	249,000	4,280	6,160	2,470
20	2,010	5.1	26,200	792	972	399
30	599	2.4	5,230	241	286	121
40	241	1.4	1,560	99	119	52
50	118	0.98	606	50	61	28
60	66	0.77	283	29	36	16.7
70	41	0.70	150	18	24	11.2
80	27	0.72	88	12	17	7.9
90	19	0.89	55	8.7	12	5.9
100	14	1.45	37	6.4	9.3	4.5

Table 4-5: Predicted Activity Coefficients for Solvents in Co-solvent/Water Mixtures

System	Methanol/Water		Acetone/Water		Ethanol/Water		Propanol/Water	
Solute	Methanol	Water	Acetone	Water	Ethanol	Water	Propanol	Water
Organic Co-solvent [% vol.]								
0	2.24	1.00	11.47	1.00	7.63	1.00	20.08	1.00
10	1.75	1.01	4.98	1.04	3.43	1.04	5.25	1.07
20	1.47	1.04	3.01	1.14	2.16	1.26	2.64	1.20
30	1.30	1.09	2.17	1.27	1.62	1.34	1.79	1.36
40	1.19	1.14	1.73	1.43	1.35	1.36	1.42	1.54
50	1.12	1.20	1.47	1.63	1.20	1.50	1.24	1.72
60	1.07	1.27	1.30	1.89	1.12	1.64	1.13	1.92
70	1.03	1.34	1.18	2.27	1.06	1.80	1.07	2.13
80	1.01	1.42	1.09	2.88	1.03	1.98	1.03	2.37
90	1.00	1.51	1.03	4.09	1.01	2.22	1.01	2.69
100	1.00	1.56	1.00	7.36	1.00	2.66	1.00	3.25

sequence for either water or methanol as the solvent. No specific trend is evident between activity coefficient in pure solvent and solute refractive index or dielectric constant. Although, it is noted that among all the solvents, the largest values of activity coefficients are observed for water as the solvent, and that water has the highest value of refractive index and dielectric constant among the various solvents. Further, least values of activity coefficients for o-xylene, naphthalene, and naphthol were observed for acetone as solvent, and that acetone has the largest dipole moment and least polarity among the various solvents. Aside from these general observations and some of the trends with naphthalene and phenanthrene solubility as discussed in a following section, there does not appear to be an obvious correlation between estimated value of solute activity coefficient with solute or solvent physical and chemical properties for the systems considered in this investigation.

Volumetric Addition Assumption

It is useful for purposes of practical environmental engineering calculations to be able to express solute concentration in terms of molar concentration (moles per liter) or mass concentration (mg or g per liter). This introduces a small difficulty because in computing molar or mass composition from activity coefficient and mole fractions, it is necessary to incorporate a value for the volume of the solute/co-solvent/water mixture. In using the activity coefficient data from Tables 4-1 to 4-5 to compute solute molar or mass concentration, it was assumed that the separate volumetric contributions of the solute, co-solvent, and water are conserved. This assumption means that the moles per unit volume of the solute/co-solvent/water mixture could be calculated from the volumetric contributions of solute, co-solvent and water, and density of pure solute, co-solvent, and water.

The validity of the assumption regarding conservation of volume can be assessed in part by comparing calculated values of the density of the co-solvent/water mixture with published values. Table 4-6 shows a comparison of observed densities of various methanol/water mixtures with values of mixture density calculated according to conservation of volume of the pure components. This comparison shows that the error in the volume addition assumption is maximum at about -3.5% for systems in the range of about 50% by weight methanol and water. The error diminishes to less than 1% for mixtures with large volumetric contribution of either co-solvent or water. The average error of this assumption for methanol/water mixtures was -2.1% with a standard deviation of 1.16%. The negative sign means that the assumption of conservation of volume slightly overestimates the volume of the co-solvent/water mixture, and therefore the computed density of the mixture was slightly underestimated by calculation of total mass divided by total pure component volume.

A similar evaluation was performed for the case of acetone/water mixtures to check the validity of the volume addition assumption. The results of the error analysis are shown in Table 4-7 for systems containing up to 11% by volume acetone. No density data were given in Weast (1983) for systems with greater than 11% by volume acetone. The largest error shown in Table 4-7 is about -1.1% for a system with about 11% by volume acetone. Average error for these data is -0.7% with a standard deviation of about -0.4%.

The magnitude of error for the volume addition assumption was evaluated for a system containing 50% volumetric contributions of acetone and water by conducting an experiment in which 500 ml of acetone and 500 ml of water were mixed in a one liter volumetric flask. After 24 hours of equilibration, it was observed that the total volume of the 50% (by volume) acetone/water mixture was 996.2 ml. This corresponds to about 0.4% overestimate assuming conservation of volume. This experiment was performed with a 50% by volume acetone/water mixture because this represented the largest volumetric contribution of acetone employed in any

Table 4-6: Error Analysis for the Volume Addition Assumption for Methanol/Water Systems

Methanol [Wt. %]	Methanol [Vol.%]	Water [Vol. %]	Mixture* Density [g/ml]	Mixture+ Density [g/ml]	Error++ [%]
1.	1.26	98.7	0.9956	0.9964	-0.08
2.	2.51	97.4	0.9930	0.9947	-0.17
4.	4.99	95.0	0.9879	0.9913	-0.34
6.	7.45	92.5	0.9828	0.9880	-0.52
8.	9.88	90.1	0.9778	0.9840	-0.63
10.	12.29	87.7	0.9728	0.9816	-0.90
12.	14.68	85.3	0.9679	0.9875	-1.99
14.	17.04	82.9	0.9630	0.9755	-1.28
16.	19.37	80.6	0.9582	0.9725	-1.47
18.	21.68	78.3	0.9534	0.9695	-1.66
20.	23.97	76.0	0.9486	0.9666	-1.86
24.	28.49	71.5	0.9393	0.9606	-2.22
28.	32.91	67.0	0.9302	0.9545	-2.55
32.	37.25	62.7	0.9212	0.9482	-2.85
36.	41.50	58.5	0.9124	0.9416	-3.10
40.	45.68	54.3	0.9038	0.9347	-3.31
44.	49.78	50.2	0.8953	0.9273	-3.45
48.	53.80	46.2	0.8870	0.9196	-3.55
52.	57.74	42.2	0.8788	0.9114	-3.58
56.	61.62	38.3	0.8708	0.9030	-3.57
60.	65.42	34.5	0.8629	0.8944	-3.52
64.	69.16	30.8	0.8552	0.8856	-3.43
68.	72.83	27.1	0.8476	0.8763	-3.28
72.	76.43	23.5	0.8401	0.8667	-3.06
76.	79.98	20.0	0.8328	0.8568	-2.80
80.	83.46	16.5	0.8256	0.8468	-2.50
84.	86.88	13.1	0.8185	0.8365	-2.15
88.	90.24	9.7	0.8116	0.8259	-1.73
92.	93.55	6.4	0.8047	0.8148	-1.23
96.	96.80	3.2	0.7980	0.8034	-0.67

Average Error = -2.1016%
Standard Deviation = 1.1638%
Total data evaluated = 59 (not all data are shown on this table)

* Calculated from volume addition assumption.
+ Observed data from Weast (1983).
++ $\left(\frac{\text{calculated value - observed value}}{\text{observed value}} \right) * 100\%$

Table 4-7: Error Analysis for the Volume Addition Assumption for Acetone/Water Systems

Acetone [Wt. %]	Acetone [Vol.%]	Water [Vol. %]	Mixture Density* [g/ml]	Mixture Density+ [g/ml]	Error++ [%]
1.	1.26	98.74	0.9956	0.9968	-0.12
2.	2.51	97.49	0.9930	0.9954	-0.24
3.	3.76	96.24	0.9904	0.9940	-0.36
4.	5.00	95.00	0.9878	0.9926	-0.48
5.	6.24	93.76	0.9852	0.9912	-0.60
6.	7.46	92.54	0.9827	0.9899	-0.73
7.	8.69	91.31	0.9801	0.9866	-0.66
8.	9.90	90.10	0.9776	0.9874	-0.99
9.	11.11	88.89	0.9751	0.9861	-1.12

Average Error = -0.65556%

Standard Deviation = 0.37454%

* Calculated from volume addition assumption.

+ Observed data from Weast (1983).

++ $\left(\frac{\text{calculated value - observed value}}{\text{observed value}} \right) * 100\%$

of the experiments, and because the methanol density data in Table 4-6 suggested that largest error in the volume addition assumption may be observed when co-solvent and water are mixed in approximately equal proportions.

It was concluded from these evaluations that the assumption of conservation of volume in co-solvent/water mixtures introduced a small error when computing system volume. However, as shown later this error is small in comparison to error introduced in estimation of solute activity coefficient.

Another reason for neglecting volume change upon mixing is the uncertainity that is introduced when considering co-solvent/water systems having appreciable concentration of solute. In this investigation all mass concentration calculations were performed in a manner to account for the volume of the solute in the co-solvent/water mixture. This consideration is especially important for those several systems containing a large percentage of co-solvent which demonstrate strong solute solubilization properties. No information is available on solution density for the solute/co-solvent/water systems evaluated in this investigation. For this reason, and also because only limited density data are available for the solute-free co-solvent/water systems, it was assumed that volumetric additions were conserved when computing solute concentration in units of mass per unit volume of solution. It should be appreciated, however, that thermodynamic calculations which employ mole fractions require no assumption regarding conservation of volume of pure components in a solution mixture.

In summary, it is recognized that the volume of a solution of nonelectrolytes is not strictly equal to the sum of the volume of individual components. Nonetheless, the small volume changes that may occur on mixing were ignored. This assumption is often made in simple theories pertaining to thermodynamic properties of mixtures of nonelectrolytes (Hildebrand et al. 1970).

Solute Solubility in Pure Solvent

The solubilities of seven aromatic solutes in five pure solvent systems were evaluated. This included the experimental measurement of the solubility of naphthalene, naphthol, quinoline and 3,5-dichloroaniline in water, and naphthalene solubility in 100% (by volume) methanol. Published values for the following systems were also considered:

- Naphthalene in water: 30 mg/l (Dean, 1973; Stephen and Stephen, 1963; Seidell, 1941), 31.7 mg/l (Mackay and Shiu, 1977),
- Naphthalene in methanol: 78,100 mg/l (Stephen and Stephen, 1963), 86,900 mg/l (Seidell, 1941),
- Naphthalene in ethanol: 95,000 mg/l (Dean, 1973), 83,600 (Stephen and Stephen, 1963), 95,200 mg/l (Seidell, 1941),
- Naphthalene in propanol: 74,300 mg/l (Seidell, 1941), 97,800 mg/l (Stephen and Stephen, 1963),
- Naphthalene in acetone: 334,000 mg/l (Stephen and Stephen, 1963),
- Naphthol in water: 866 mg/l (Hassett et al., 1981), 713 mg/l (Stephen and Stephen, 1963), 740 mg/l (Seidell, 1941),
- Quinoline in water: 6,100 mg/l (Neely and Mackay, 1982)
- Aniline in water: 36,600 mg/l (Stephen and Stephen, 1963), 36,100 mg/l (Seidell, 1941),
- Phenanthrene in water: 1.29 mg/l (Mackay and Shiu, 1977), 2.9 mg/l (Stephen and Stephen, 1963),
- Phenanthrene in methanol: 27,600 mg/l (Gmehling et al. 1978), 24,500 mg/l (Stephen and Stephen, 1963); 28,000 mg/l (Seidell, 1941),
- Phenanthrene in ethanol: 31,700 mg/l (Stephen and Stephen, 1963), Gmehling et al., 1978), 33,000 mg/l (Seidell, 1941), and
- o-Xylene in water: 196 mg/l (Stephen and Stephen, 1963), 130 mg/l (Seidell, 1941). Note: 1,2-dimethylbenzene.

Experimental and reported solute solubilities in pure solvents are compared with predicted values of solute solubility in this section. In order to estimate the solute solubility in a pure solvent, the required input parameters are the activity coefficient of the solute in the solvent, the heat of mixing of the solute, the solute molecular weight, and the melting point of the solute. The technique for estimating the activity coefficient was the UNIFAC approach, from which the activity coefficient can be related to solubility by use of either Equation 2-31 and 2-32 (Hildebrand, 1950) or Equation 2-30 (Prausnitz, 1969). Both of these techniques are discussed below.

If the solute exists as a solid at the system temperature, the heat of fusion of the solute can be taken as the heat of mixing. The value of the heat of fusion at the melting point for some of the chemical compounds used in this work are available (Weast, 1983). If the heat of fusion for a solid solute is not available, heat of fusion can be estimated by using entropy of fusion multiplied by melting point temperature in °K. An average value of entropy of fusion for solid organic compounds has been found to be 13 cal/mole °K (Prausnitz, 1969; Yalkowsky, 1979). If the heat capacities of solid and liquid phase for the solid solute are available, then the variation of heat of fusion with temperature should be considered, as provided in Equation 2-32 (Hildebrand, 1950). Alternatively, mole fraction solute solubility can be computed as given in Equation 2-30 (Prausnitz, 1969). Both of these approaches will be considered with respect to naphthalene and naphthol solubility in water, methanol, and acetone. Table 4-8 lists the necessary physical properties which are required to perform these and other calculations for the solutes and solvents employed in the investigation. The approach given by Equations 2-31 and 2-32 will be considered first, for which the heat of fusion of naphthalene is found from Equation 2-32 to be 4767 cal/mole. The activity coefficient of naphthalene in water is 139,000, from which the mole fraction solubility of naphthalene in water can be estimated by Equation 2-37 as 2.04×10^{-6}, and from this the solubility of naphthalene in water can be calculated as 14.5 mg/l. The activity coefficient for naphthalene in methanol is 13.03, and thus the mole fraction naphthalene solubility in methanol can be estimated by Equation 2-38 by trial and error as 0.0245, or 77,600 mg/l. The activity coefficient for naphthalene in acetone is 2.53, and

Table 4-8: Physical and Chemical Properties of Solutes and Solvents Employed for Solute Solubility Calculations*

	Molecular Weight [g/mole]	Melting Point [°C]	Density [g/ml]	Molar Volume [ml/mole]	Heat of Fusion [cal/mole]
Solutes:					
Naphthalene	128.19	80.5	0.9625	133.18	4540
Naphthol	144.19	96	1.0989	131.21	5610
Quinoline	129.16	15.6	1.0929	118.18	-
3,5-Dichloroaniline	162.02	51-53 (52)**	1.2859	126	3750
Aniline	93.12	-6.3	1.0217	91.49	-
Phenanthrene	178.24	96.3	0.9800	181.88	4450
o-Xylene	106.17	-25.2	0.880	120.62	-
Solvents:					
Water	18.02	0	0.9971	18.07	-
Methanol	32.04	-93.9	0.7914	40.4852	-
Acetone	58.08	-95.4	0.7899	73.5283	-
Ethanol	46.07	-117.3	0.7893	58.37	-
Propanol	60.11	-126.5	0.8035	74.81	-

* After Weast (1983).

** Melting point in a range of 51 and 53°C, 52°C was used in this study.

Note: ΔC_p for naphthalene is 5.04 cal/mole °K

ΔC_p for naphthol is 28.59 cal/mole °K thus the mole fraction solubility of naphthalene in acetone can be estimated by trial and error by solving Equation 2-38 as 0.178, or 276,000 mg/l.

In an analogous manner, Equation 2-30 can be used to estimate naphthalene and naphthol solubility in water, methanol and acetone. For the case of naphthalene solubility in pure solvents, the first term of Equation 2-30, $\frac{\Delta H_f}{RT}\ [1 - \frac{T}{T_f}]$ is calculated as 1.204, the second term, $[-(\frac{\Delta C_p}{RT})\ (T_f - T)]$, is calculated to be -0.473 and the third term, $\frac{\Delta C_p}{R} \ln \frac{T_f}{T}$, is calculated as +0.433. Note that the second term and the third term tend to cancel each other. After substitution of these values into Equation 2-30, the naphthalene mole fraction solubility in water is found as 2.25×10^{-6} (16.1 mg/l). Similarly, naphthalene mole fraction solubility in methanol is estimated as 0.0239 (82,800 mg/l), and naphthalene mole fraction solubility in acetone is estimated as 0.123 (187,000 mg/l).

Table 4-9 shows the solubilities of naphthalene and naphthol in different solvents as calculated by Equation 2-30 and Equation 2-31. The results show that both approaches give similar results for predicting solubility from an estimate of activity coefficient. The calculation approach given by Equation 2-31, in conjunction with Equation 2-32 if ΔC_p data are available, was selected for estimating solubility from activity coefficient because of the ease of computation and because of the similarity of the computed results with Equation 2-30 as shown in Table 4-9.

Table 4-10 shows values of solute solubilities in pure solvents, where the predicted solute solubilities were calculated from estimation of infinite dilution activity coefficient via the UNIFAC model with Equations 2-37 to 2-41. For the four solid solutes considered in this study, i.e., naphthalene, naphthol, 3,5-dichloroaniline, and phenanthrene, the infinite dilution activity coefficients for these solutes in water are 139,000, 486, 878, and 7,410,000,

Table 4-9: Comparison of Calculation Procedures for Estimation of Solute Solubility in Pure Solvents

Solute	Solvent	Solubility of Solute			
		Equation 2-30		Equations 2-31, 2-32	
		X_2	[mg/l]	X_2	[mg/l]
Naphthalene	Water	2.26×10^{-6}	16.1	2.04×10^{-6}	14.5
Naphthalene	Methanol	0.0278	82,800	0.0245	77,600
Naphthalene	Acetone	0.123	187,000	0.178	271,000
Naphthol	Water	4.73×10^{-4}	3,780	1.72×10^{-4}	1,370
Naphthol	Methanol	0.127	352,000	0.1265	351,000
Naphthol	Acetone	0.245	792,000	0.218	705,000

Note: X_2: mole fraction solute solubility [-]

[mg/l]: solute solubility as mass concentration

Table 4-10: Solute Solubilities in Pure Solvents

Solute	Solvent	Solute Solubility	
		Prediction X_2 (C_2)	Observed X_2 (C_2)
Naphthalene	Water	2.26×10^{-6} (16.1)	4.27×10^{-6} (30.6)$^{+}$
Naphthalene	Methanol	0.0278 (82,800)	0.0220 (66,200)$^{+}$
Naphthalene	Acetone	0.178 (271,000)	0.227 (334,000)*
Naphthalene	Ethanol	0.0402 (88,300)	0.0459 (95,200)$^{++}$
Naphthalene	Propanol	0.0525 (93,400)	0.0577 (97,800)*
Naphthol	Water	1.72×10^{-4} (1,380)	1.06×10^{-4} (846)$^{+}$
Naphthol	Methanol	0.1265 (351,000)	NA
Naphthol	Acetone	0.218 (365,000)	NA
Quinoline	Water	5.44×10^{-4} (3,900)	9.57×10^{-4} (6,840)$^{+}$
Quinoline	Methanol	1.0 (1,090,000)	NA
Quinoline	Acetone	1.0 (1,090,000)	NA
3,5-Dichloroaniline	Water	8.17×10^{-5} (735)	7.72×10^{-5} (692)$^{+}$
3,5-Dichloroaniline	Methanol	0.603 (1,060,000)	NA
3,5-Dichloroaniline	Acetone	0.573 (896,000)	NA
Aniline	Water	0.011 (56,900)	6.66×10^{-3} (34,100)*
Aniline	Methanol	1.0 (1,020,000)	NA
Aniline	Ethanol	1.0 (1,020,000)	NA
Phenanthrene	Water	3.156×10^{-8} (0.31)	2.9×10^{-7} (1.29)**
Phenanthrene	Methanol	0.0098 (43,100)	0.00571 (24,500)*
Phenanthrene	Ethanol	0.016 (48,900)	0.0106 (31,700)*
o-Xylene	Water	1.77×10^{-5} (104)	3.33×10^{-5} (196)*
o-Xylene	Methanol	1.0 (880,000)	NA
o-Xylene	Acetone	1.0 (880,000)	NA
o-Xylene	Ethanol	1.0 (880,000)	NA
o-Xylene	Propanol	1.0 (880,000)	NA

X_2 = mole fraction solute solubility [-]
C_2 = Mass concentration in mg/l, as shown in parenthesis
+: experimental data from this study
++: taken from Seidell (1941)
*: taken from Stephen and Stephen (1963)
**: taken from Mackay and Shiu (1977)
NA: not available

respectively. These activity coefficients are greater than 100, thus Equation 2-37 is used to estimate the solid solute solubility in water. The infinite dilution activity coefficients for naphthalene in methanol and ethanol are 13.0 and 14.0 respectively, and that for phenanthrene in methanol and ethanol are 25.5 and 36.9 respectively. Since these activity coefficients are between 10 and 100, Equation 2-38 is then used to calculate the solute (naphthalene and phenanthrene) solubilities in methanol and ethanol. The infinite dilution activity coefficients for naphthalene in acetone and propanol are 2.58 and 9.30 respectively, and that for naphthol in methanol and acetone are 0.79 and 0.17 respectively. These activity coefficients are less than 10, therefore Equation 2-37 was employed with a trial and error calculation to calculate solute solubility. The heat of fusions for the solid solutes were corrected for the heat capacity terms if the data were available. The heat capacity of solid and liquid for naphthalene were known, and ΔC_p was calculated as 5.04 cal/mole °K; the heat of fusion at 25°C was then calculated from Equation 2-32 as 4,767.4 cal/mole. The same procedure was used for naphthol, where ΔC_p is calculated as 28.59 cal/mole °K, and the heat of fusion is determined as 7,645 cal/mole by using Equation 2-32. Heat capacity data for phenanthrene are not available; therefore, the heat of fusion for phenanthrene was taken as 4,450 cal/mole without correction.

The results in Table 4-10 show reasonable agreement between predicted and experimental solute solubility in pure solvents. The ratio of predicted aqueous solubility versus observed experimental values are all within a factor of two except for phenanthrene where aqueous solubility is predicted to be 0.3 mg/l compared to a measured value of about 1.3 mg/l. Solute solubility in pure co-solvent was predicted within about ±50% for those solutes for which experimental data were available. No comparison of liquid solute (e.g., quinoline, aniline, and o-xylene) solubilities in pure methanol, ethanol, acetone or propanol were made because literature values were not available. Neither were experimental measurements attempted to measure these solute solubilities in those solvents owing to difficulties in sample preparation and because of constraints on the instrument detection limit. The infinite dilution activity coefficient for quinoline and aniline in pure methanol were estimated as 1.8, and 2.5 respectively. Therefore, based on the discussion in Chapter 2, it was concluded that quinoline and aniline are infinitely soluble with methanol. Similar conclusions were made for quinoline in acetone (γ_2^{∞} = 2.6), o-xylene in acetone (γ_2^{∞} = 2.2), aniline in ethanol (γ_2^{∞} = 1.45), o-xylene in ethanol (γ_2^{∞} = 6.4), and o-xylene in propanol (γ_2^{∞} = 4.5). For the case of o-xylene solubility in methanol, the infinite dilution activity coefficient is 9.6, which is greater than 7.4; therefore, Equation 2-41 was used to estimate solute solubility. The results of this procedure were plotted as $\Delta G^M/RT$ versus solute mole fraction solubility, and only one minimum was observed. Thus it was concluded that o-xylene is completely miscible with methanol. For these liquid solutes in pure organic co-solvent, the mole fraction solubility approaches unity and the concentration of the solute in the mixed solution can be assumed to approach the pure liquid solute concentration.

The results of solute solubilities in pure solvents show for a non-polar aromatic solute (i.e., naphthalene and phenanthrene) that solubility increases with decrease in solvent polarity. For example, naphthalene solubility in water, methanol, ethanol, and propanol increases as 30.6, 66,200, 95,200, and 97,800 mg/l respectively, and solute polarity (E_T value from Table 2-3) decreases for water, methanol, ethanol, and propanol in the order 63.1, 53.5, 51.9, and 50.7 Kcal/mole respectively. Likewise phenanthrene solubility increases in the order of water (1.3 mg/l), methanol (24,500 mg/l), and ethanol (31,700 mg/l).

Solute Solubility in Solvent/Water Mixtures

The solubility of solutes in co-solvent/water mixtures was evaluated by four approaches: the log-linear approach, the UNIFAC approach, the excess free energy approach, and the molecular surface area approach. Prediction and experimental data for the eighteen systems investigated are displayed as semi-log plots in Figures 4-1 through 4-18. The standard deviations for the experimental data determined in this study were presented Chapter 3 and are not shown on the figures. In general the coefficient of variations for these data lie within the range of 2 and 15% of the average value and would not be noticeably discernible from the indicated data points. The abscissa of these plots is the volume fraction of the co-solvent, and the ordinate is the solute solubility in units of mg/l. A tabulation of these solubility prediction data is given in Appendix B. The best-fit curves for the log-linear, UNIFAC, excess free energy and molecular surface area predictions for the co-solvent/water systems were performed using polynomial curve fitting for predictions calculated from 0% to 100% by volume co-solvent in 5% by volume increments. The log-linear approach was plotted as solid line, the UNIFAC approach as dashed line, the excess free energy approach as chain-dotted line, and the molecular surface area approach as a chain-dashed line. The procedures used for these calculations were described in Chapter Two, and additional information required for the computational procedures is discussed following some general comments.

A general observation on the results of the solubility of the aromatic solutes in the various co-solvent/water mixtures is that solute solubility increases semi-logarithmically with increase of volume fraction of organic co-solvent. This is illustrated by linear regression of the experimental data obtained in this investigation, as shown in Figures 4-19 and 4-20 where the expressions for the regression equation are given in units of mg/l, not g/l as plotted. For the case of naphthalene, naphthol, quinoline, and 3,5-dichloroaniline, Figure 4-19 shows the semi-logarithmic linear regression

Figure 4-1: **Naphthalene Solubility in Methanol/Water Mixtures**

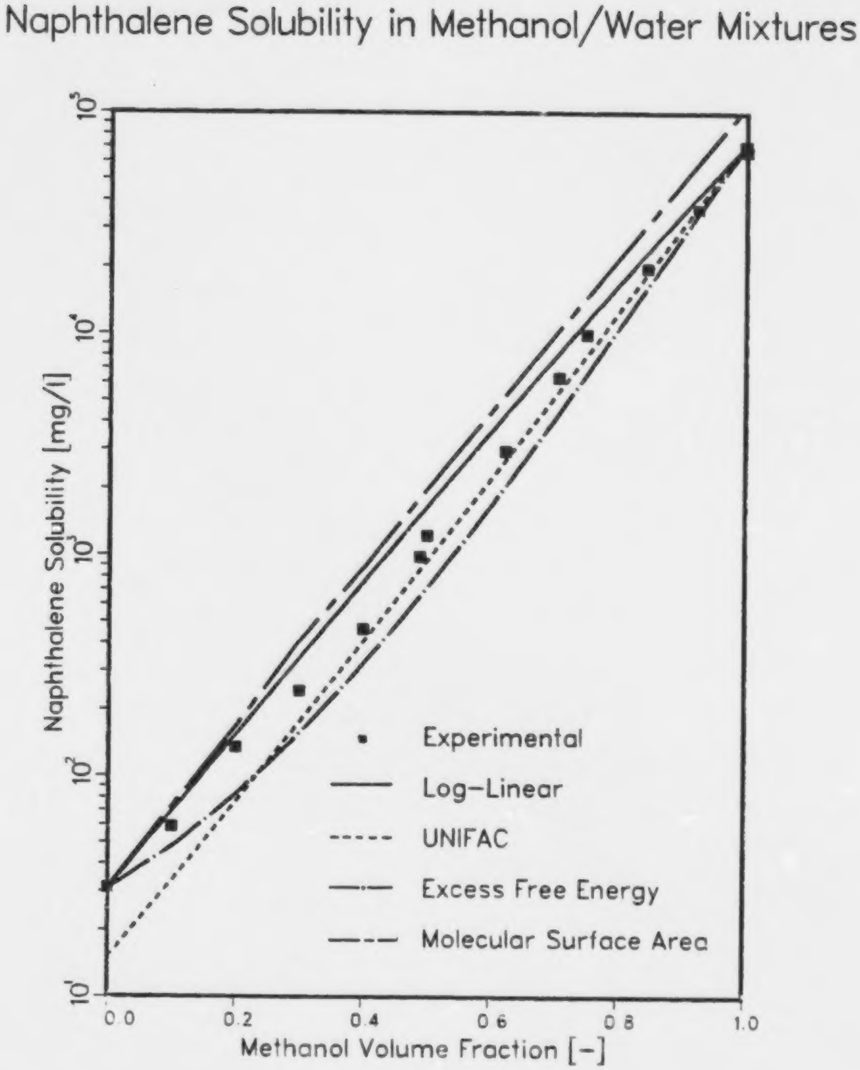


Figure 4-2: Naphthalene Solubility in Acetone/Water Mixtures

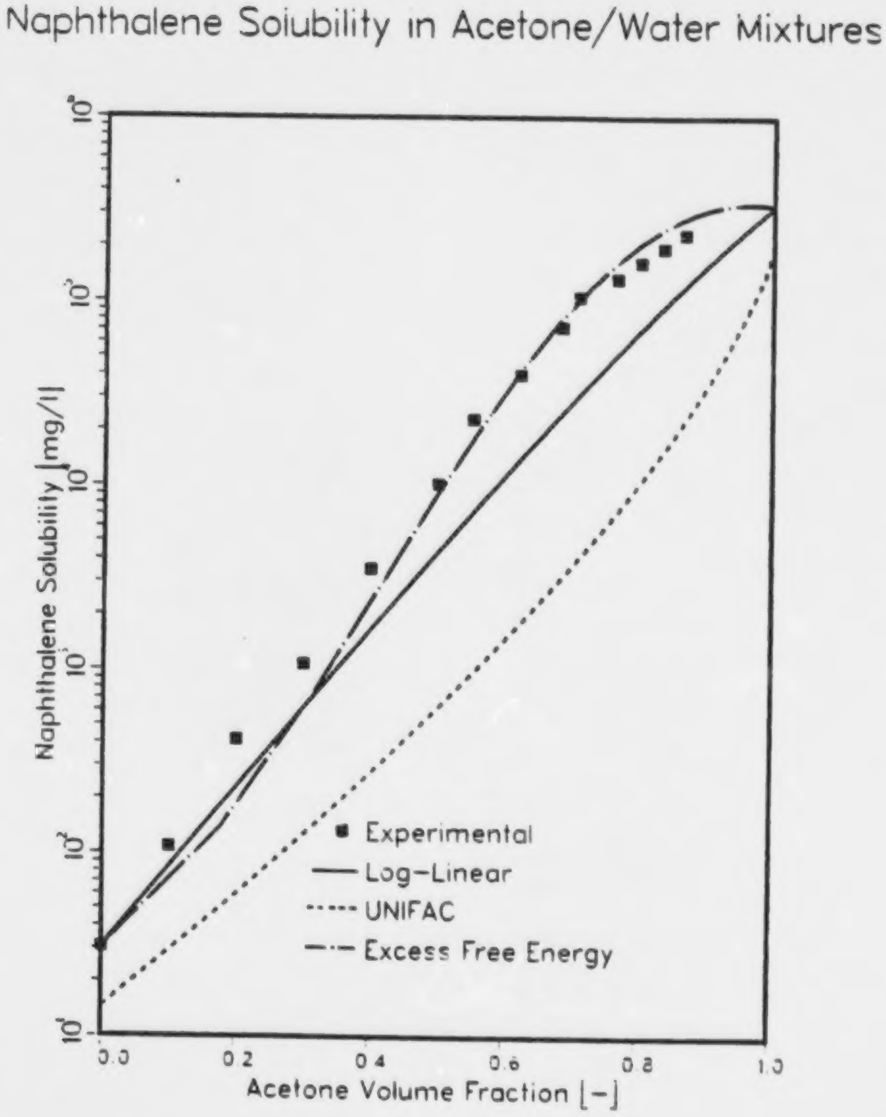


Figure 4-3: Naphthalene Solubility in Ethanol/Water Mixtures

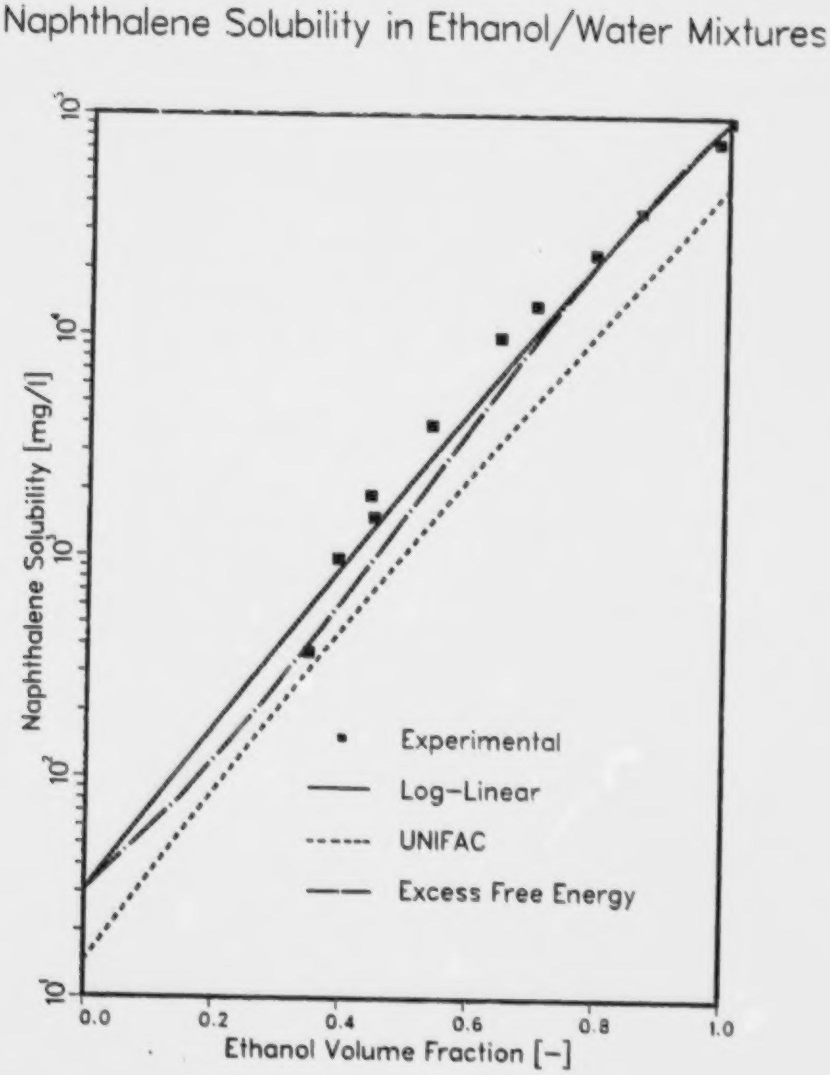


Figure 4-4: Naphthalene Solubility in Propanol/Water Mixtures

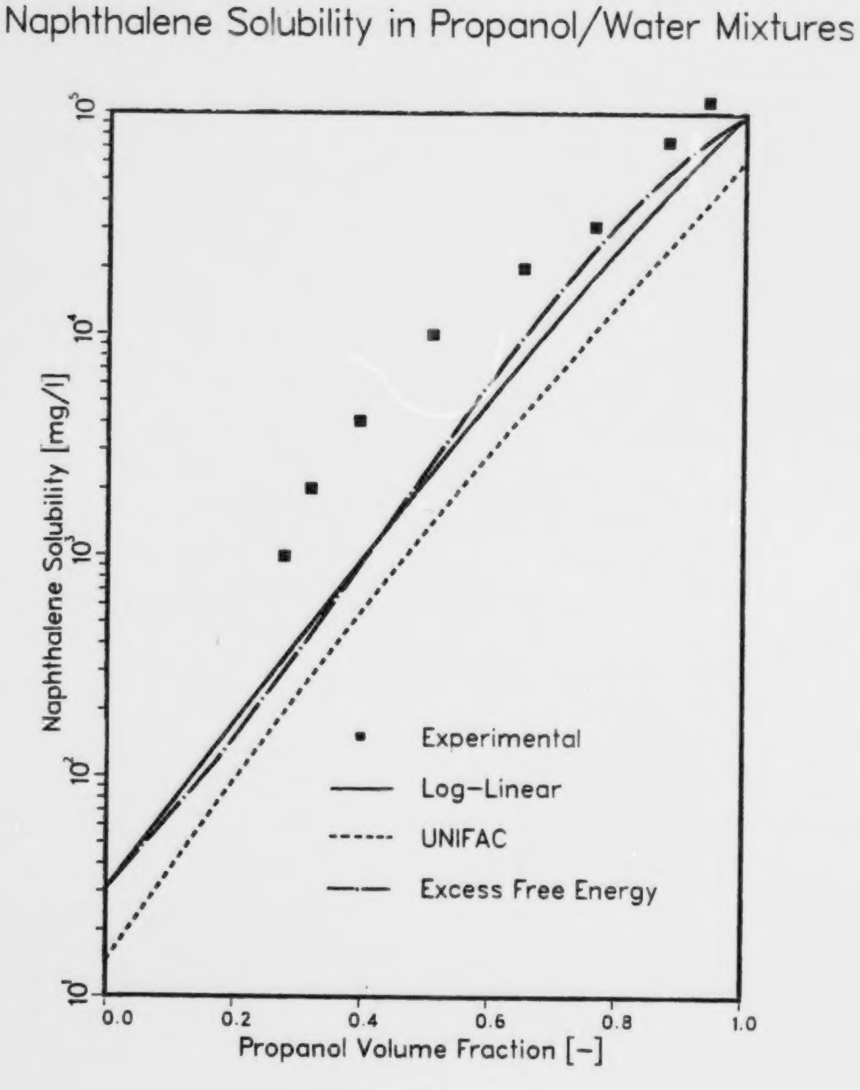


Figure 4-5: **Naphthol Solubility in Methanol/Water Mixtures**

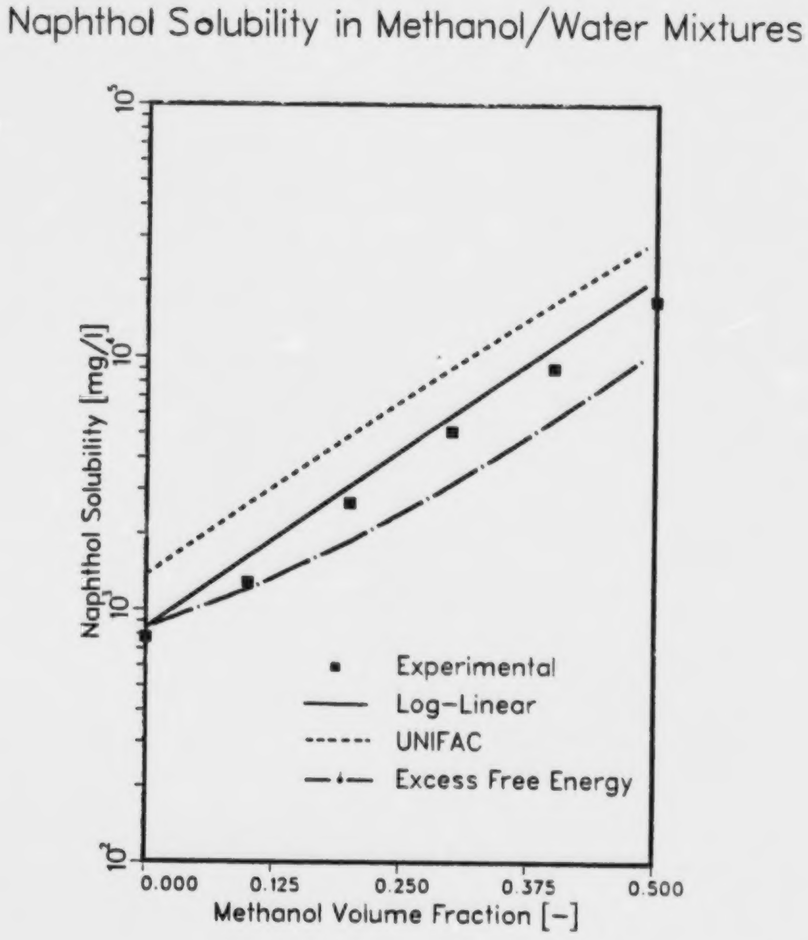


Figure 4-6: **Naphthol Solubility in Acetone/Water Mixtures**

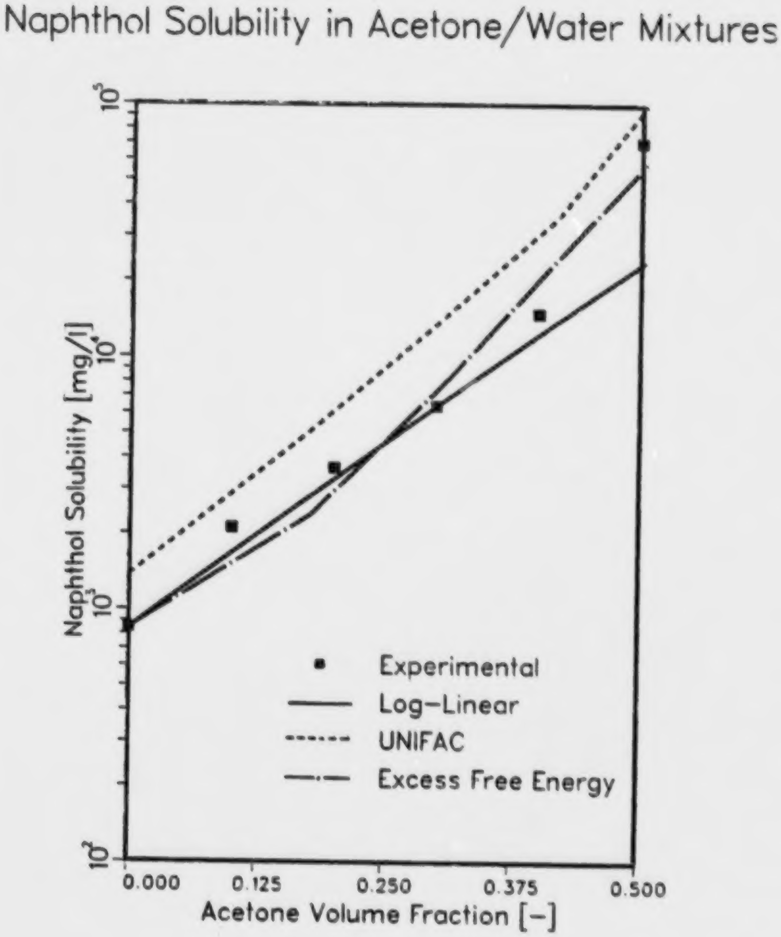


Figure 4-7: Quinoline Solubility in Methanol/Water Mixtures

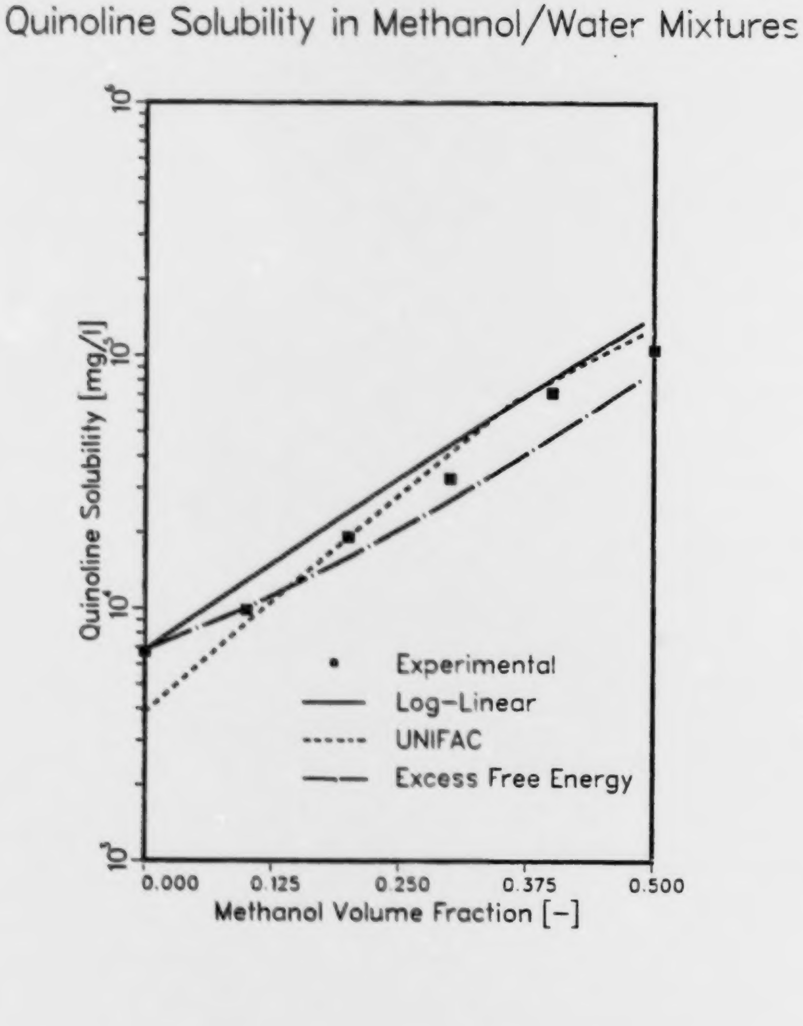


Figure 4-8: **Quinoline Solubility in Acetone/Water Mixtures**

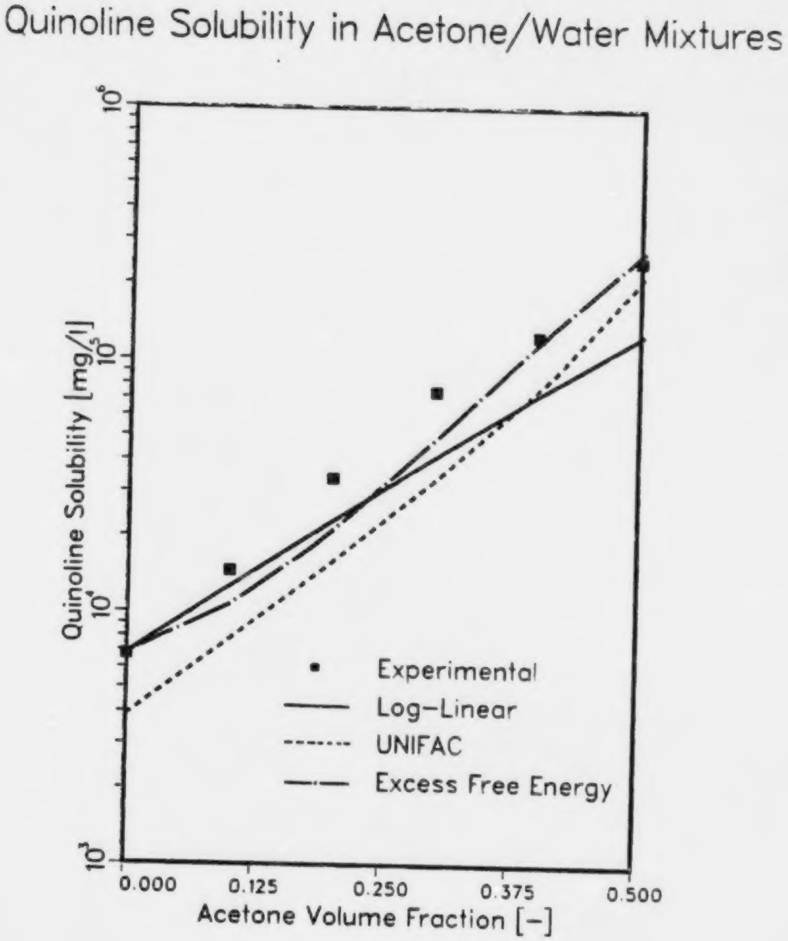


Figure 4-9: 3,5-Dichloroaniline Solubility in Methanol/Water Mixtures

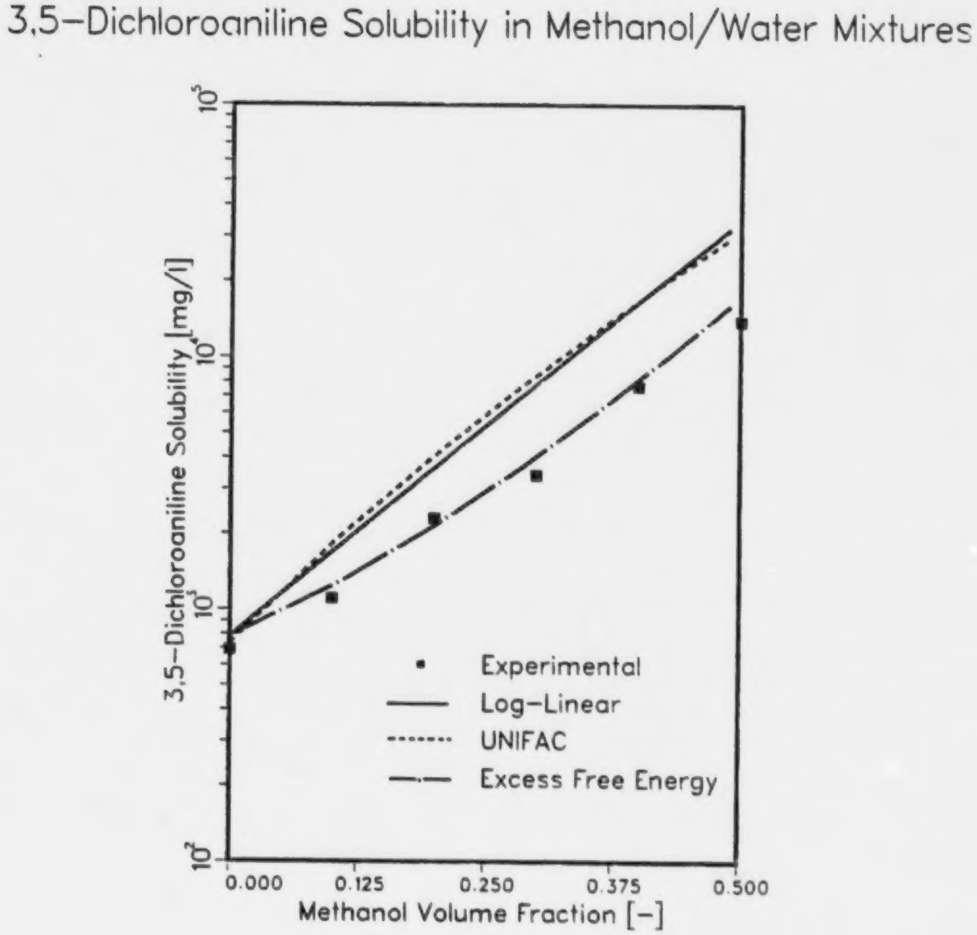


Figure 4-10: 3,5-Dichloroaniline Solubility in Acetone/Water Mixtures

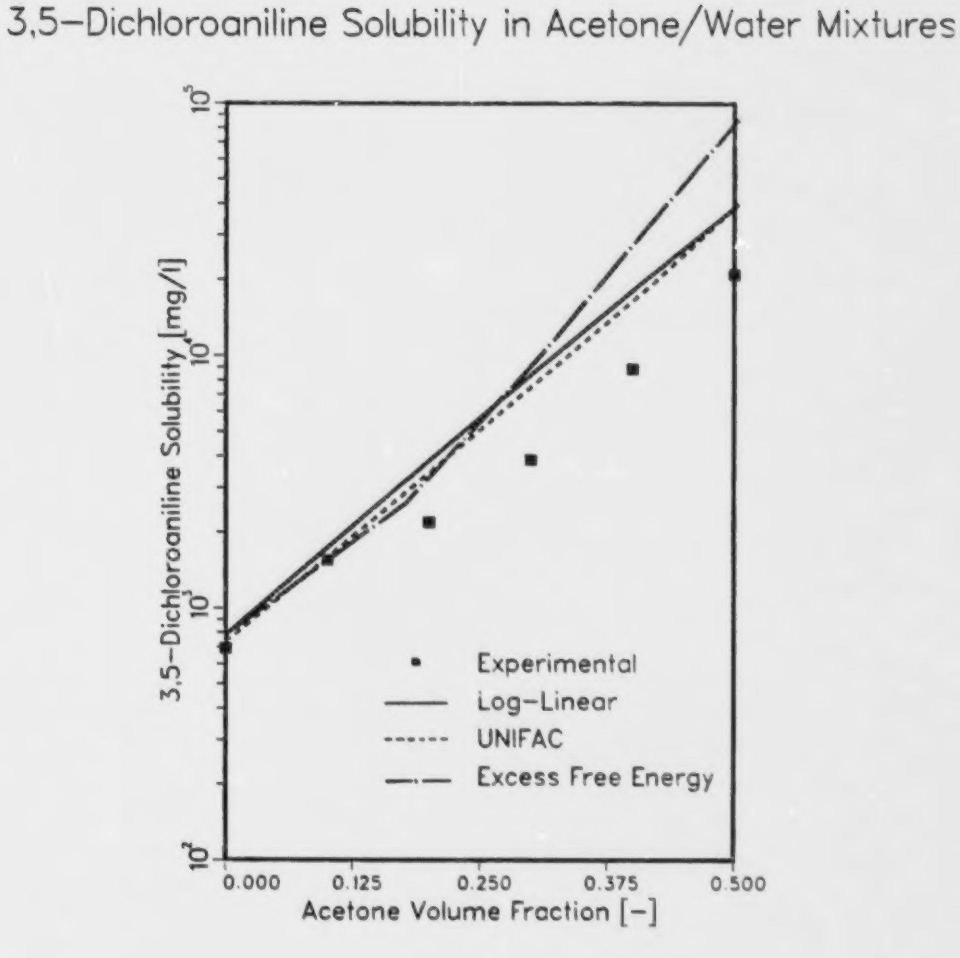


Figure 4-11: **Aniline Solubility in Methanol/Water Mixtures**

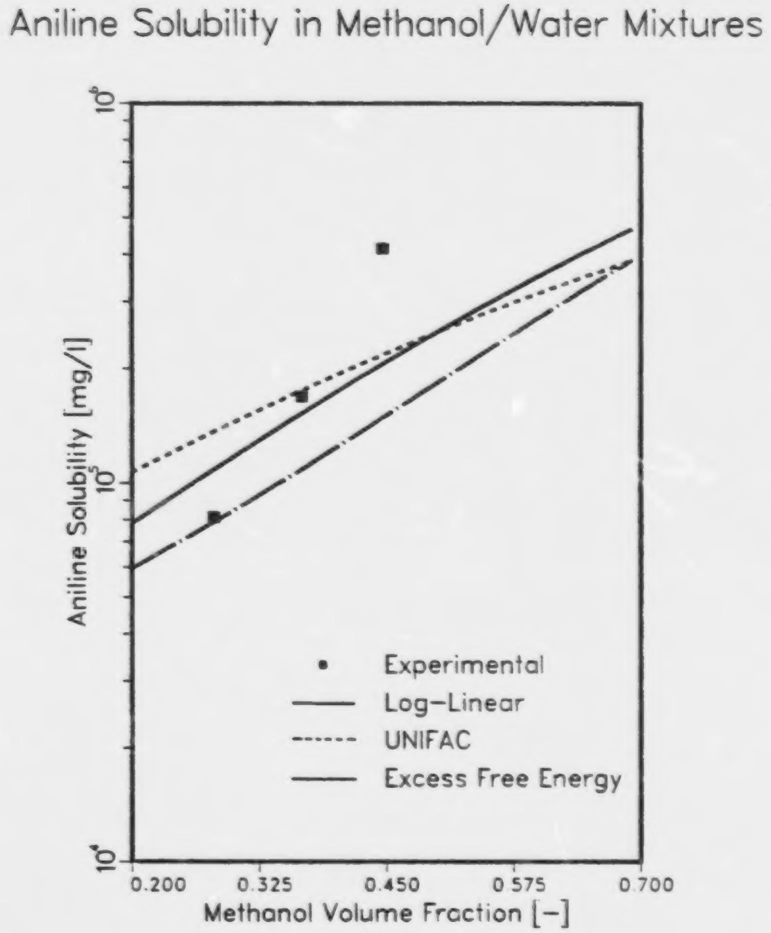


Figure 4-12: Aniline Solubility in Ethanol/Water Mixtures

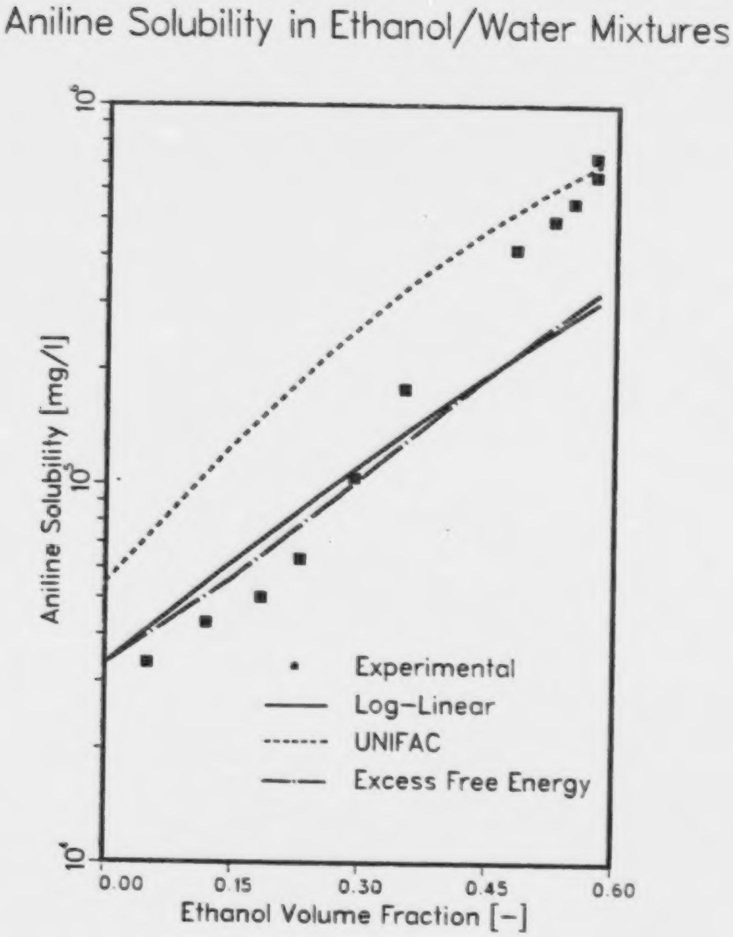


Figure 4-13: Phenanthrene Solubility in Methanol/Water Mixtures

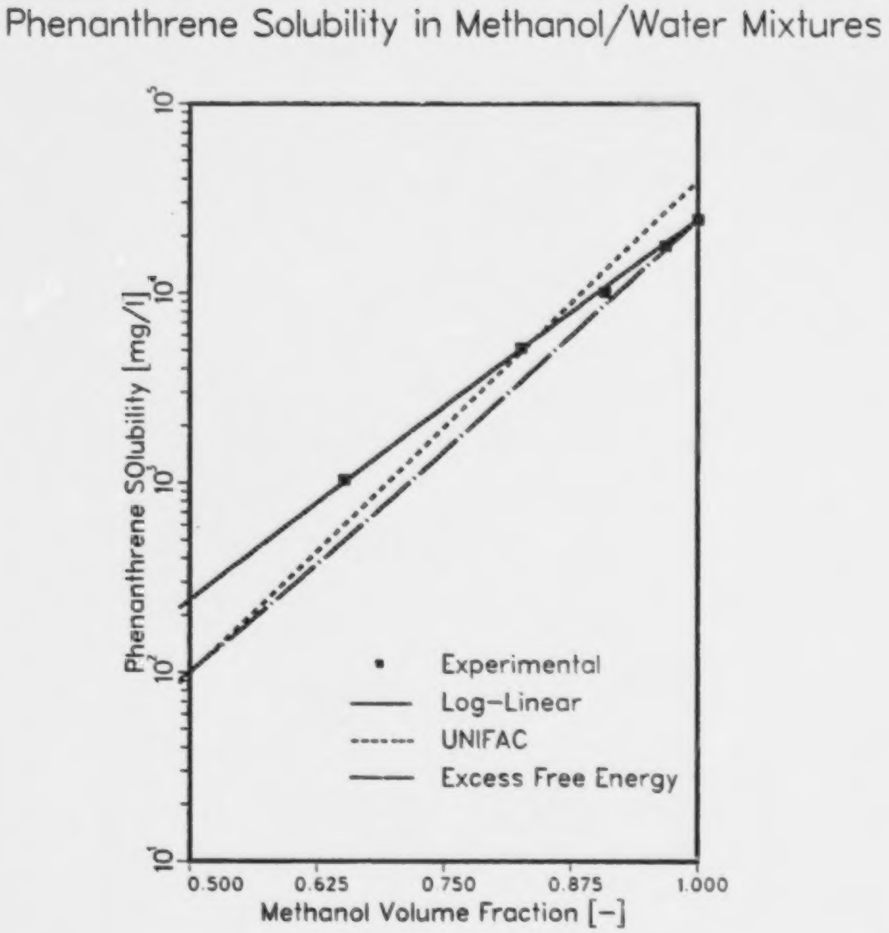


Figure 4-14: Phenanthrene Solubility in Ethanol/Water Mixtures

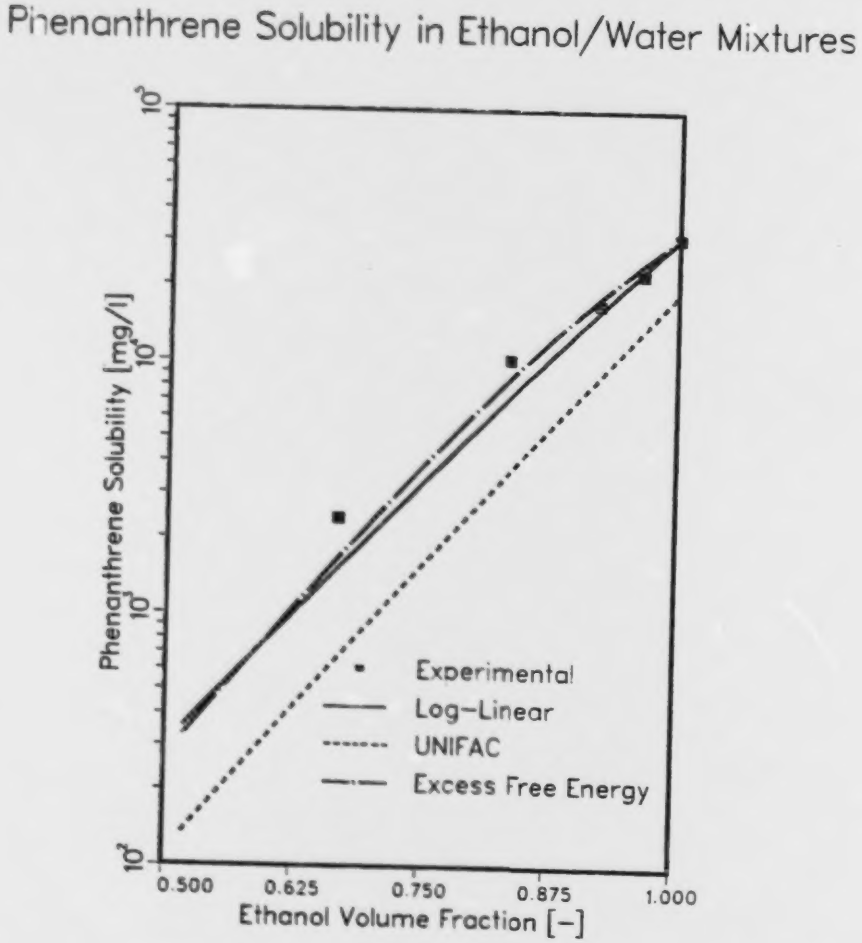


Figure 4-15: o-Xylene Solubility in Methanol/Water Mixtures

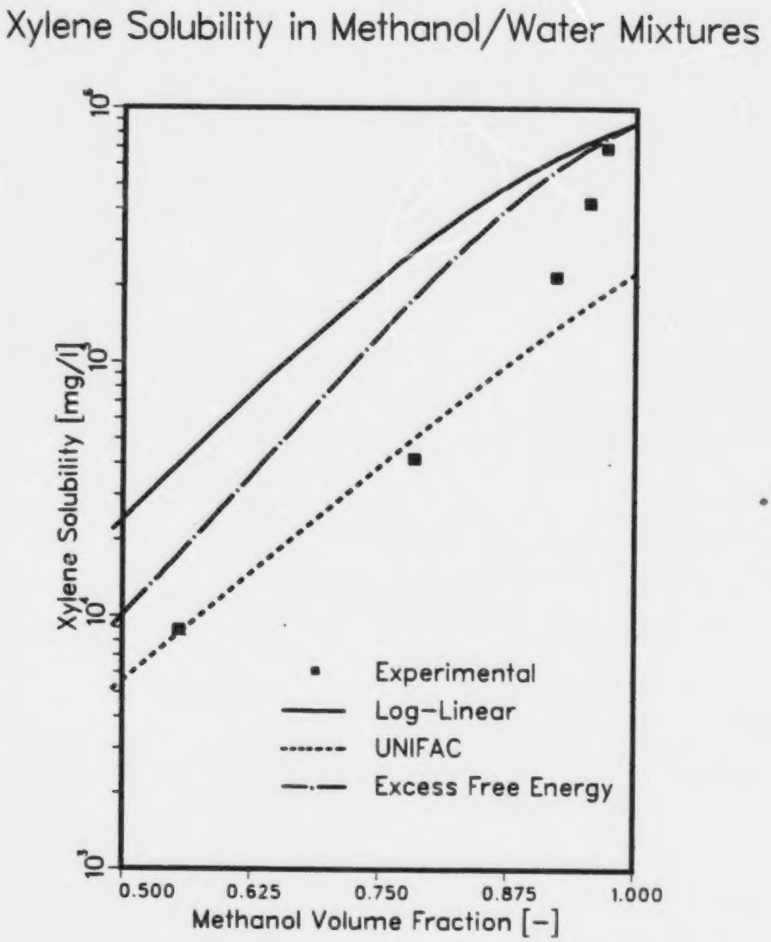


Figure 4-16: o-Xylene Solubility in Acetone/Water Mixtures

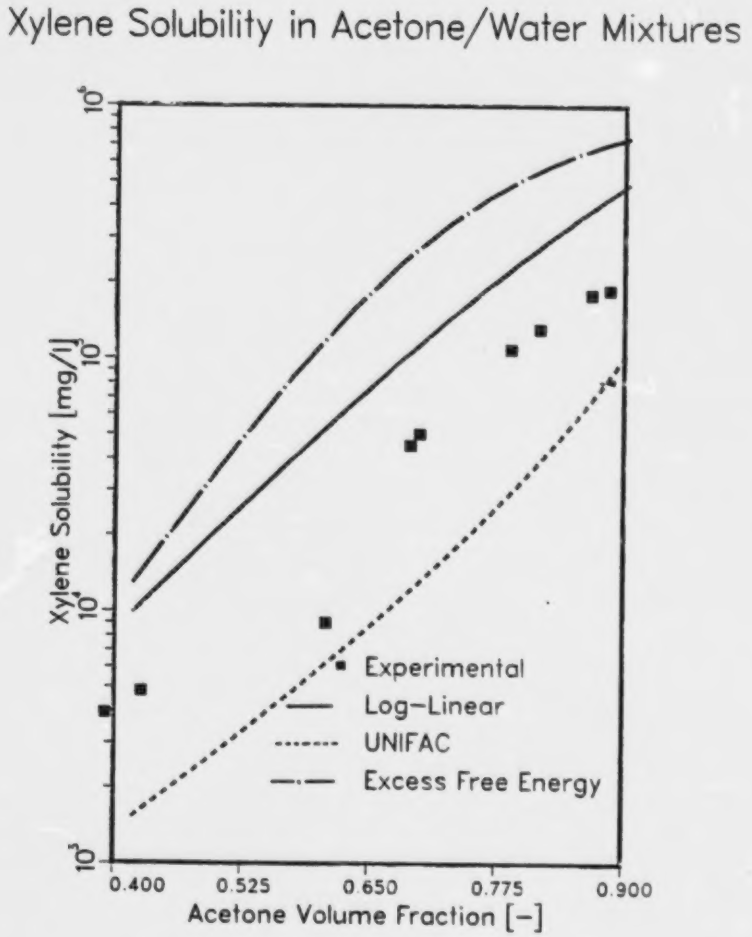


Figure 4-17: o-Xylene Solubility in Ethanol/Water Mixtures

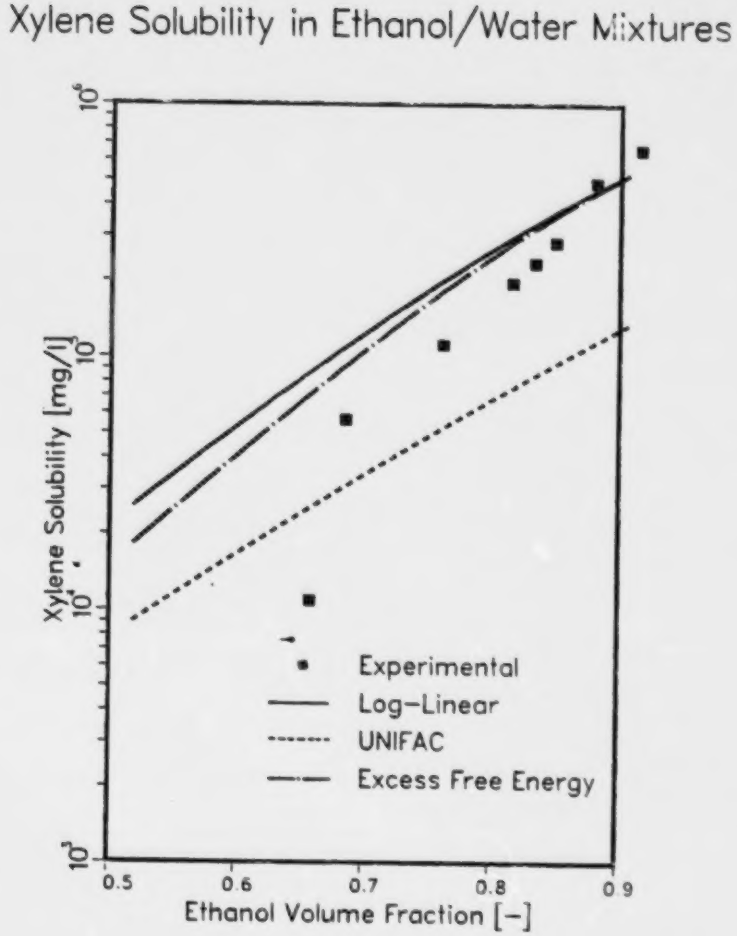


Figure 4-18: o-Xylene Solubility in Propanol/Water Mixtures

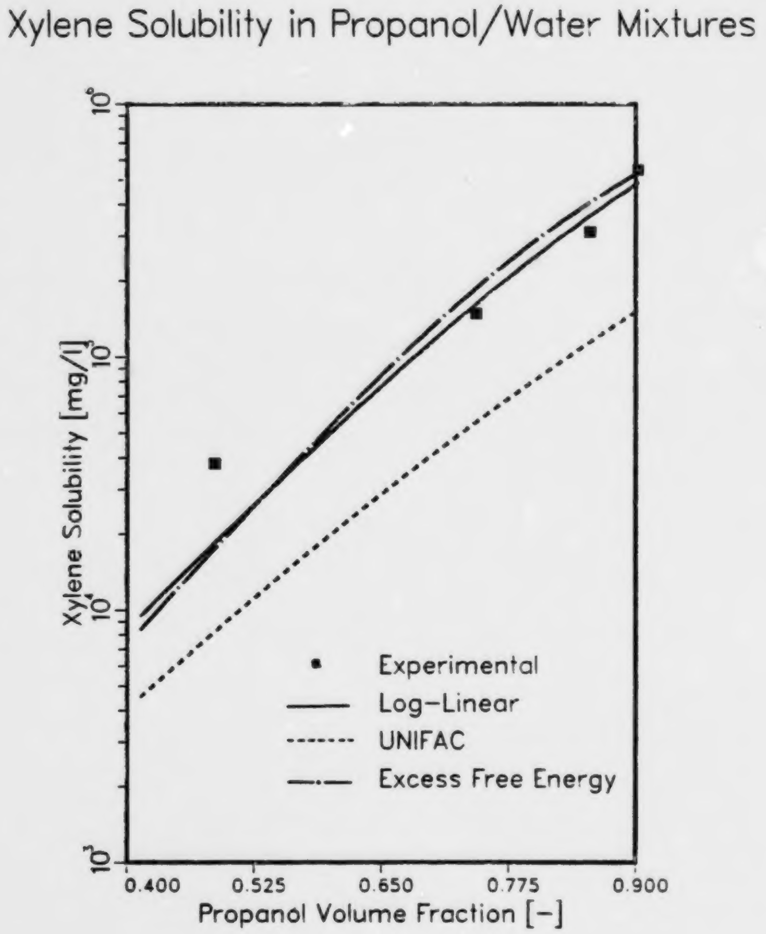
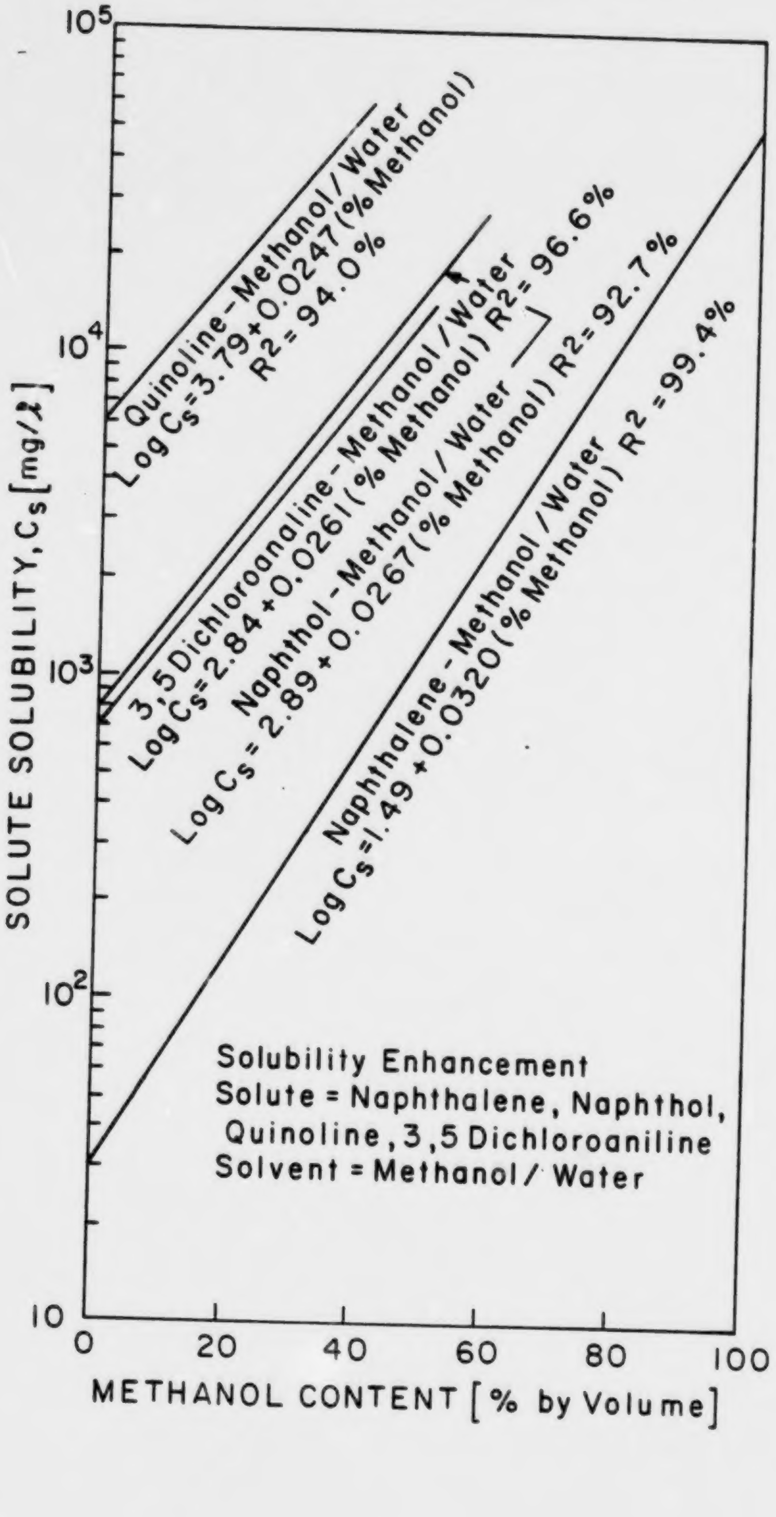


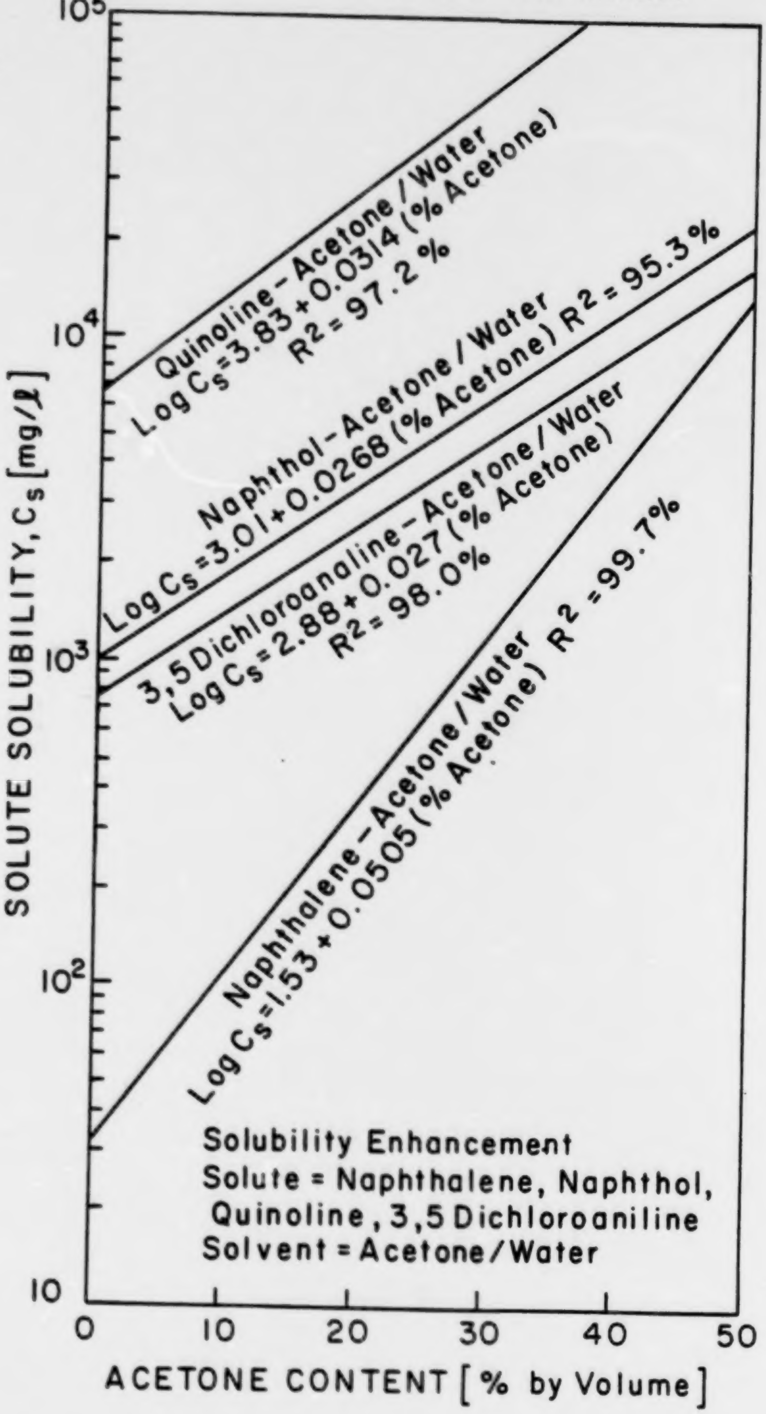
Figure 4-19: Linear Regression for Solute Solubility in Methanol/Water Mixtures



results for the four solutes in methanol/water systems, and Figure 4-20 shows the semi-logarithmic linear regression results for the four solutes in acetone/water systems. The slopes of the regression lines in Figures 4-19 and 4-20 show the magnitude of solubility enhancement with increased solvent content. Figure 4-19 shows the slopes for naphthalene, naphthol, quinoline, and 3,5-dichloroaniline in methanol/water mixtures are 3.20, 2.67, 2.47, and 2.61 respectively. Figure 4-20 shows the slopes for naphthalene, naphthol, quinoline, and 3,5-dichloroaniline in acetone/water mixtures are 5.05, 2.70, 3.14, and 2.47 respectively. The regression coefficient and r^2 values are also shown in Figures 4-19 and 4-20. The eight experimental systems show excellent r^2 values, which range from 92.7% for naphthol solubility in methanol/water mixtures to 99.7% for naphthalene solubility in acetone/water mixtures. The linear regression results indicate that the data can be reasonably well represented by a log-linear relationship.

The log-linear approach for predicting solute solubility in co-solvent/water mixtures was evaluated for the eighteen systems. This was performed by taking the difference of the log of solute solubility in water (mg/l or g/l) and the log of solute solubility in pure co-solvent as the constant σ, and then calculating solute solubility according to Equation 2-78. Experimental or literature data were used for solubility in 100% water. Experimental or literature data were used for solubility in 100% co-solvent, if available as shown in Table 4-10. Otherwise solubility in 100% co-solvent was taken as that estimated by the UNIFAC approach. The magnitude of increase in solubility (corresponding to σ in Equation 2-78) for naphthalene, naphthol, quinoline, and 3,5-dichloroaniline in methanol/water systems by the log-linear approach was found to be 3.34, 2.65, 2.20, and 2.97 respectively. The magnitude of increase in solubility for naphthalene, naphthol, quinoline, and 3,5-dichloroaniline in acetone/water systems by the log-linear approach was found to be 4.04, 2.64, 2.19, and 3.05 respectively. These values agree with the linear regression coefficients for the eight experimental systems. The magnitude of increase in phenanthrene solubility in methanol was found

Figure 4-20: Linear Regression for Solute Solubility in Acetone/Water Mixtures



to be 4.44, which is greater than that found for naphthalene (3.34). This suggests that the more hydrophobic the solute the greater the solubility would be enhanced with increase of fraction co-solvent.

The excess free energy approach for estimating solute solubility in solvent/water mixtures was evaluated also for the eighteen systems. In order to use this approach three parameters had to be determined: solvent interaction parameters $A_{1\text{-}3}$ and $A_{3\text{-}1}$, and the solute-solvent interaction parameter, C_2. The solvent interaction parameters $A_{1\text{-}3}$ and $A_{3\text{-}1}$ were determined from estimation of activity coefficients for the co-solvent and water using the UNIFAC procedure and a two-parameter statistical regression technique with Equation 2-76. The results of this procedure showed that these two parameters are constants for any of the binary solvent systems considered in this investigation. Table 4-11 summarizes the values of $A_{1\text{-}3}$ and $A_{3\text{-}1}$ and the standard deviation and r^2 values for the four different co-solvent/water systems. It is concluded from the results shown in Table 4-11 that the $A_{1\text{-}3}$ and $A_{3\text{-}1}$ terms are co-solvent specific constants. Once the solvent interaction parameters were determined, the solute-solvent interaction parameter, C_2, was calculated from Equation 2-73 using the experimental data, except for that data for solute solubility in the pure co-solvent and water. The statistical analysis showed that for the eighteen systems investigated in this study and the eight systems investigated by Williams and Amidon (1984c), that C_2 can be correlated with solute K_{ow} by

$$C_2 = -2.87 - 2.29 \log K_{ow} \qquad r^2 = 69.1\% \qquad (4\text{-}6)$$

This value of r^2 indicates reasonable agreement, although not as good as other relationships evaluated in this study.

The values of $A_{1\text{-}3}$, $A_{3\text{-}1}$ and C_2 were then used to predict solute solubility in co-solvent/water mixtures. In these predictions the value of C_2 was taken as that given by Equation 4-6. The value of C_2 was not taken as an individual, system-specific regression parameter because it was desired to assess the generality of the approach. The results in Figure 4-1 through 4-18

Table 4-11: Solvent Interaction Parameters for the Binary Solvent Systems

Co-solvent/water System	A_{1-3}	A_{3-1}	Standard Deviation	r^2
Methanol - Water	0.771	0.460	0.000738	100%
Ethanol - Water	1.67	0.766	0.001122	100%
Propanol - Water	2.59	0.966	0.001320	100%
Acetone - Water	1.86	1.18	0.000903	99.8%

show that the excess free energy approach accounts for some of the deviation from the log-linear relationship. This is also demonstrated later under discussion of error analysis.

In order to calculate solute solubility in solvent/water mixtures by the molecular surface area approach, several parameters must be known: hydrophobic and polar surface areas, HSA and PSA, and microscopic interfacial free energy densities for water and solvent, $\Delta\epsilon_h$ and $\Delta\epsilon_p$ respectively. Of the eighteen systems evaluated in this investigation, naphthalene solubility in methanol/water mixtures was the only system for which the four input parameters were available. It may be assumed for naphthalene that the compound is relatively nonpolar and that the polar surface area is small compared to the hydrophobic surface area; therefore, polar surface area may be neglected and the total surface area may be represented by the hydrophobic surface area. Yalkowsky et al. (1976) reported that the hydrophobic surface area for naphthalene is 155.8 $\mathring{A}^2$ and that the microscopic interfacial free energy density for methanol and water is 23.7 dyne/cm, thus the parameter σ in Equation 2-76 can be evaluated as 3.893. It is found that this constant for naphthalene solubility in methanol/water systems shows reasonable agreement with σ values evaluated by the log-linear approach (σ=3.34) and the linear-least-square fit of experimental data (σ=3.20). Naphthalene solubility in water is experimentally determined as 30.6 mg/l with which the solubility of naphthalene in methanol/water mixtures can be calculated by Equation 2-92. The results of prediction of naphthalene solubility in methanol/water mixtures by the molecular surface approach are presented in Table 4-12, where the bias is 218% with an accuracy of 248%. The molecular surface area approach can not be evaluated for the other systems because not all of the values of HSA, PSA, $\Delta\epsilon_h$, and $\Delta\epsilon_p$ are available.

Table 4-12: Naphthalene Solubility in the Methanol/Water System Using the Molecular Surface Area Approach

Methanol [% Vol.]	Experimental Solubility [mg/l]	Predicted Solubility [mg/l]	Error
Experimental Values			
.010	39.1	32.2	-.084
.050	46.5	37.7	-.091
.099	59.0	75.7	.108
.199	135.0	186.0	.139
.299	243.0	455.0	.272
.399	463.0	1120.0	.384
.499	1230.0	2740.0	.348
1.000	66900.0	244000.0	.562
Reported Values			
.488	986.0	2490.0	.402
.622	2960.0	8240.0	.445
.706	6360.0	17500.0	.440
.749	9960.0	25700.0	.412
.844	19800.0	60300.0	.484
.924	36600.0	123000.0	.526
.996	70600.0	237000.0	.526
.998	71100.0	241000.0	.530

Bias = 218%
Accuracy = 248%
Number of Points Evaluated = 16
Note: Perfection prediction corresponds to bias = 100% and accuracy = 100%

Error Analysis for Solute Solubility in Solvent/Water Mixtures

An error analysis was performed in order to evaluate the various approaches for predicting solute solubility in co-solvent/water systems. Since the data for the systems evaluated experimentally in this study show a logarithmic increase in solute solubility with increase in solvent volume fraction, it was decided that the most appropriate procedure for performing the error analysis was to compute error and root mean square error in logarithmic space. The bias and accuracy are then given by antilogs of the average error and root mean square error respectively. Thus error is computed as

$$\text{Error} = y = \log (C_{predicted}) - \log (C_{experiment}) \qquad (4\text{-}7)$$

The average error is computed as

$$\bar{y} = \frac{\sum_{i=1}^{n} (\log C_{predicted} - \log C_{experiment})}{n} \qquad (4\text{-}8)$$

where n is the number of experimental data. The bias is computed as the antilog of $\bar{y}$

$$\text{Bias } [\%] = 10^{\bar{y}} * 100\% \qquad (4\text{-}9)$$

where a bias of 100% represents perfect prediction. The root mean square error is computed as

$$\text{rms } (y) = \left(\frac{\sum_{i=1}^{n} (\log C_{predicted} - \log C_{experiment})^2}{n} \right)^{1/2} \qquad (4\text{-}10)$$

and the accuracy is given as

$$\text{Accuracy } [\%] = 10^{rms(y)} * 100\% \qquad (4\text{-}11)$$

where an accuracy of 100% represents perfect estimation. Note that the accuracy is analogous to standard deviation, and it is always represented by a value greater than 100%. The error analysis was performed individually for each system using all experimentally available or reported data. Table 4-12 presented the error analysis for the molecular surface area approach for naphthalene solubility in methanol/water mixtures. Appendix C presents the error analysis for the other three approaches for each of the 18 systems investigated.

Table 4-13 summarizes the results of the error analysis for the UNIFAC approach. The average error by UNIFAC approach ranged from -0.001 for quinoline solubility in 20% methanol/80% water to -1.423 for naphthalene solubility in 21% acetone/79% water. The bias by the UNIFAC approach is 65.3% which corresponds to an overall average error of -0.185, with a accuracy of 321%. The negative sign on the overall average error indicates that on the average the UNIFAC approach underestimated solute solubility in co-solvent/water mixtures. The UNIFAC approach underestimated the solute solubility in twelve co-solvent/water systems and overestimated solute solubility in six co-solvent/water systems. The accuracy of the prediction was generally in the range of 150 to 400%, except for the naphthalene-acetone/water system.

Table 4-14 summarizes the results of the error analysis for the excess free energy approach. The average error by the excess free energy approach ranged from 0.002 for naphthalene solubility in 86.2% ethanol/13.8% water to -0.956 for o-xylene solubility in 66% ethanol/34% water. The overall average error was -0.039, which corresponds to a bias of 91.5%. The negative sign on the overall average error means that the excess free energy approach underpredicted the solute solubility in the co-solvent/water mixtures. The accuracy was 174%. The excess free energy approach tended to underestimate solute solubility for twelve of the eighteen co-solvent/water systems.

Table 4-15 summarizes the results of the error analysis for the log-

Table 4-13: Error Analysis of Solute Solubility Prediction in Solvent/Water Mixtures by the UNIFAC Approach

Solute	Solvent	Bias [%]	Accuracy [%]
Naphthalene	Methanol	81.1	148
Naphthalene	Acetone	7.29	1450
Naphthalene	Ethanol	45.6	227
Naphthalene	Propanol	21.2	495
Naphthol	Methanol	177	178
Naphthol	Acetone	167	172
Quinoline	Methanol	96.8	130
Quinoline	Acetone	56.3	186
3,5-Dichloroaniline	Methanol	179	190
3,5-Dichloroaniline	Acetone	160	170
Aniline	Methanol	97.1	161
Aniline	Ethanol	442	460
Phenanthrene	Methanol	76.9	272
Phenanthrene	Ethanol	45.9	232
o-Xylene	Methanol	69.5	194
o-Xylene	Acetone	201	337
o-Xylene	Ethanol	81.6	153
o-Xylene	Propanol	57.0	246
Overall		65.3	321

Number of Points Evaluated = 122

Note: Perfection prediction corresponds to bias = 100% and accuracy = 100%

Table 4-14: Error Analysis of Solute Solubility Prediction in Solvent/Water Mixtures by the Excess Free Energy Approach

Solute	Solvent	Bias [%]	Accuracy [%]
Naphthalene	Methanol	69.8	149
Naphthalene	Acetone	76.7	149
Naphthalene	Ethanol	74.8	152
Naphthalene	Propanol	40.1	285
Naphthol	Methanol	73.9	144
Naphthol	Acetone	92.4	130
Quinoline	Methanol	85.2	124
Quinoline	Acetone	78.1	138
3,5-Dichloroaniline	Methanol	126	131
3,5-Dichloroaniline	Acetone	207	246
Aniline	Methanol	60.6	191
Aniline	Ethanol	121	121
Phenanthrene	Methanol	80.0	142
Phenanthrene	Ethanol	92.6	121
o-Xylene	Methanol	156	178
o-Xylene	Acetone	316	321
o-Xylene	Ethanol	130	200
o-Xylene	Propanol	92.7	153
Overall Number of Points Evaluated = 122		91.5	174

Note: Perfection prediction corresponds to bias = 100% and accuracy = 100%

Table 4-15: Error Analysis of Solute Solubility Prediction in Solvent/Water Mixtures by the Log-linear Approach

Solute	Solvent	Bias Error [%]	Accuracy Square [%]
Naphthalene	Methanol	118	125
Naphthalene	Acetone	38.0	275
Naphthalene	Ethanol	88.5	132
Naphthalene	Propanol	36.8	132
Naphthol	Methanol	117	119
Naphthol	Acetone	76.1	160
Quinoline	Methanol	123	126
Quinoline	Acetone	62.2	167
3,5-Dichloroaniline	Methanol	204	222
3,5-Dichloroaniline	Acetone	174	183
Aniline	Methanol	84.4	156
Aniline	Ethanol	131	132
Phenanthrene	Methanol	101	103
Phenanthrene	Ethanol	84.6	130
o-Xylene	Methanol	192	238
o-Xylene	Acetone	217	217
o-Xylene	Ethanol	137	215
o-Xylene	Propanol	85.7	146
Overall		95.7	187

Number of Points Evaluated = 122

Note: Perfection prediction corresponds to bias = 100% and accuracy = 100%

linear approach. The average error by the log-linear approach ranged from -0.046 for naphthol solubility in 30% acetone/70% water to 1.041 for o-xylene solubility in 66% ethanol/34% water. The overall average error for the log-linear predictive approach was -0.019 which corresponds to a bias of 95.7%. The accuracy for the log-linear approach was 187%. The log-linear approach tended to overestimate solute solubility for ten of the eighteen co-solvent/water systems.

Comparison of the overall average error for the 18 systems investigated in this study shows that the UNIFAC approach underpredicted 12 systems, the excess free energy approach underpredicted 12 systems, and the log-linear approach overestimated 10 systems. The bias for the three approaches decreased in the order: the UNIFAC approach (65.4%), the excess free energy approach (91.5%), and the log-linear approach (95.7%). The accuracy for the three approaches improved in the order: the UNIFAC approach (321%), the log-linear approach (187%), and the excess free energy approach (174%). Therefore, it may be concluded that these three approaches gave somewhat different results for the eighteen systems investigated. The excess free energy approach showed the best accuracy. Therefore, this procedure represents the most reliable procedure for predicting solute solubility in co-solvent/water mixtures. It should be recalled however, that the excess free energy approach required the use of solute solubility in pure water and pure solvent, as well as two parameters estimated from the UNIFAC procedure and a third parameter obtained from correlation of experimental data. The input data for the log-linear approach required experimental values of aqueous solubility and measured or estimated (by UNIFAC) solubility in 100% solvent. The accuracy of this approach was not substantially worse than that given by the excess free energy approach. Comparison of the success with which solute solubility may be predicted showed that the more experimental data or correlation coefficients that are employed, the more reliable the results. The UNIFAC approach performed especially well in consideration that no experimental measurements are required in order to make the prediction. The log-linear approach is obviously the simplest technique to apply, and it is attractive if some experimental co-solvent/water solubility data are available.

Solubility Parameter and Solubility in Co-solvent/Water Mixtures

The solubility parameter, δ, is used as a characteristic parameter to describe solute and solvent properties, and in certain instances it can be used to make qualitative predictions on solute solubility. The solubility parameter was defined in Chapter Two, and Table 2-4 showed the values of solubility parameters for the solutes and solvents used in this investigation. The solubility parameter approach for predicting solute solubility was evaluated for naphthalene and phenanthrene because these compounds are comparatively non-polar, non-hydrogen bonding. Thus among the various solutes investigated in this study, they most closely satisfy the basic requirements for regular solution theory in which the principal solution interaction consists of dispersion forces.

Hildebrand and Scatchard (Hildebrand and Scott, 1950) developed regular solution theory which explains that the solubility of a solid, whose solution obeys Raoult's law, can be expressed as Equation 2-93. The activity of the solid solute can be taken as that for the subcooled liquid, which is equal to the ideal solubility of the solid solute, X_2^i, so Equation 2-93 becomes

$$\ln \frac{X_2^i}{X_2} = \frac{V_2 z_1^2}{RT} (\delta_1 - \delta_2)^2 \tag{4-12}$$

This is the Hildebrand-Scatchard solubility equation for a solid compound, with solubility parameter δ_2, dissolved in a solvent with solubility parameter δ_1. For purposes of this discussion, the volume fraction of the solvent mixture (z_1) is taken as the sum of the volume fractions of co-solvent and water. As a first approximation, the solubility of naphthalene and phenanthrene in water and co-solvents may be assumed small, and thus the volume contribution of the solute is small compared to the volume fraction of the co-solvent and water; therefore it was assumed that $z_1 = 1$. This assumption does not introduce appreciable error, because except for naphthalene solubility in acetone, mole fraction solubility is less than approximately 2%. The ideal solute solubility can be calculated from the heat of fusion of the solid solute at the melting point and the heat capacities of the solid and subcooled liquid (Equation 2-32), and

$$\ln X_2^i = -\frac{\Delta H_f}{RT}\left(\frac{T_m - T}{T_m}\right) \tag{4-13}$$

or

$$\ln X_2^i = -\frac{\Delta S_f}{R}\ln\left(\frac{T_m}{T}\right) \tag{4-14}$$

The solubility parameter for the co-solvent/water mixture is calculated from Equation 2-94. For a multicomponent system, Hildebrand and Scott (1950) suggest that the solubility parameter is simply the volume fraction weighed arithmetic mean of solubility parameters of the pure component (Equation 2-94). For example, the solubility parameter for pure water is 23.50 and the solubility parameter for methanol is 15.15; therefore, the solubility parameter for 50% (by volume) methanol and water mixture can be calculated as 19.3. The evaluation of the solubility parameter approach was performed using Equations 4-12, 4-13 and 2-94 for naphthalene solubility in methanol/water and acetone/water systems, and for phenanthrene solubility in methanol/water and ethanol/water systems. Tables 4-16 and 4-17 show the results of the solubility parameter approach for predicting solubility of naphthalene in methanol/water and acetone/water mixtures respectively. Tables 4-18 and 4-19 show the results of the solubility parameter approach for predicting phenanthrene solubility in methanol/water and ethanol/water mixtures. The observed naphthalene and phenanthrene solubility data are also shown in Tables 4-16 through 4-19 for comparison.

The results in Tables 4-16 to 4-19 show that predicted solubility

Table 4-16: Solubility Parameter and Solubility of Naphthalene in Methanol/Water Mixtures

Naphthalene solubility parameter = 9.9
Water solubility parameter = 23.50
Methanol solubility parameter = 15.15

Fraction [Wt.]	Fraction [vol.]	$\bar{\delta}^*$	Observed Solubility [-]	Predicted solubility [-]
.0000	.0000	23.50	.211E-05	.673E-17
.0472	.1007	22.66	.494E-05	.726E-15
.1003	.2013	21.82	.120E-04	.578E-13
.1604	.3017	20.98	.261E-04	.338E-11
.2292	.4020	20.14	.731E-04	.147E-09
.3084	.5021	19.31	.183E-03	.471E-08
.4008	.6020	18.47	.466E-03	.112E-06
.5099	.7017	17.64	.120E-02	.197E-05
.6408	.8013	16.81	.323E-02	.258E-04
.8005	.9007	15.98	.878E-02	.251E-03
.2992	.4912	19.40	.731E-04	.328E-08
.4240	.6247	18.28	.578E-03	.221E-06
.5174	.7080	17.59	.193E-02	.234E-05
.5716	.7511	17.23	.265E-02	.731E-05
.7076	.8455	16.44	.502E-02	.736E-04
.8446	.9248	15.78	.112E-01	.417E-03
.9928	.9968	15.18	.237E-01	.172E-02
.9969	.9986	15.16	.242E-01	.178E-02
1.000	1.000	15.15	.246E-01	.183E-02

*: Solubility parameters of methanol/water mixture, calculated from Equation 2-94

Table 4-17: Solubility Parameter and Solubility of Naphthalene in Acetone/Water Mixtures

Naphthalene solubility parameter = 9.9
Water solubility parameter = 23.50
Acetone solubility parameter = 9.93

Fraction [Wt.]	Fraction [vol.]	δ^*	Observed Solubility [-]	Predicted solubility [-]
.0000	.0000	23.50	.203E-05	.673E-17
.0266	.1004	22.14	.440E-05	.114E-13
.0578	.2004	20.78	.980E-05	.856E-11
.0952	.3006	19.42	.227E-04	.300E-08
.1406	.4006	18.06	.548E-04	.476E-06
.1971	.5007	16.71	.139E-03	.348E-04
.2691	.6006	15.35	.375E-03	.116E-02
.3642	.7006	13.99	.110E-02	.179E-01
.4953	.8004	12.64	.377E-02	.126E+00
.6884	.9002	11.28	.169E-01	.411E+00
.2320	.5524	16.00	.230E-03	.236E-03
.2874	.6223	15.06	.465E-03	.225E-02
.3470	.6846	14.21	.919E-03	.122E-01
.3749	.7101	13.86	.122E-02	.223E-01
.4457	.7666	13.10	.239E-02	.711E-01
.4974	.8017	12.62	.384E-02	.129E+00
.5541	.8354	12.16	.610E-02	.209E+00
.6157	.8675	11.73	.984E-02	.304E+00
1.000	1.000	9.93	.227E+00	.615E+00

*: Solubility parameters of acetone/water mixture, calculated from Equation 2-94

Table 4-18: Solubility Parameter and Solubility of Phenanthrene in Methanol/Water Mixtures

Phenanthrene solubility parameter = 9.8
Water solubility parameter = 23.50
Methanol solubility parameter = 15.15

Fraction [Wt.]	Fraction [vol.]	$\bar{\delta}^*$	Observed Solubility [-]	Predicted solubility [-]
.0000	.0000	23.50	.300E-07	.115E-24
.0472	.1007	22.66	.100E-06	.161E-21
.1003	.2013	21.82	.340E-06	.136E-18
.1604	.3017	20.98	.970E-06	.695E-16
.2292	.4020	20.14	.395E-05	.217E-13
.3084	.5021	19.31	.137E-04	.409E-11
.4008	.6020	18.47	.487E-04	.470E-09
.5099	.7017	17.64	.177E-03	.331E-07
.6408	.8013	16.81	.654E-03	.143E-05
.8005	.9007	15.98	.250E-02	.377E-04
.4555	.6542	18.03	.953E-04	.462E-08
.6791	.8271	15.56	.920E-03	.350E-05
.8153	.9089	15.91	.280E-02	.484E-04
.9310	.9683	15,41	.631E-02	.265E-03
1.000	1.000	15.15	.979E-02	.614E-03

*: Solubility parameters of methanol/water mixture, calculated from Equation 2-94

Table 4-19: Solubility Parameter and Solubility of Phenanthrene in Ethanol/Water Mixtures

Phenanthrene solubility parameter = 9.8
Water solubility parameter = 23.50
Ethanol solubility parameter = 13.09

Fraction [Wt.]	Fraction [vol.]	δ^*	Observed Solubility [-]	Predicted solubility [-]
.0000	.0000	23.50	.300E-07	.498E-25
.0419	.1238	22.21	.160E-06	.152E-20
.0716	.1994	21.43	.420E-06	.507E-18
.1167	.2991	20.39	.145E-05	.598E-15
.1705	.3990	19.35	.499E-05	.370E-12
.2357	.4990	18.31	.168E-04	.119E-09
.3163	.5991	17.27	.557E-04	.196E-07
.4185	.6992	16.23	.182E-03	.167E-05
.5523	.7994	15.19	.586E-03	.733E-04
.7351	.8996	14.14	.190E-02	.165E-02
.3836	.6678	16.55	.126E-03	.445E-06
.6101	.8348	14.82	.887E-03	.238E-03
.7864	.9224	13.91	.254E-02	.306E-02
.8946	.9648	13.47	.427E-02	.876E-02
1.000	1.000	13.09	.665E-02	.192E-01

*: Solubility parameters of ethanol/water mixture, calculated from Equation 2-94

deviates significantly from the observed solubility. The solubility parameter approach predicts very poorly for the solute solubility in pure water where deviations of many orders of magnitude are observed. The predicted solubility value improves as the water content decreases in the co-solvent/water mixture. For pure co-solvent, the estimated solute solubilities are within a factor of two to ten of the observed values.

Hildebrand developed the regular solution theory on the assumption that dispersive forces are the dominant solution interaction and that symmetrical interactions occur between adjacent molecules in solution. Clearly these assumptions are violated with a strongly polar, hydrogen bonding solvent like water. The assumptions are more applicable for systems comprised of 100% organic solvent, and this explains the trend toward convergence of observed and predicted solute solubility as the mixture composition increases in volume fraction co-solvent. It is concluded that the use of regular solution theory is not generally suitable for predicting solute solubility for the solute/co-solvent/water systems investigated in this study. It is recognized that a form of the regular solution equation can be used to represent solute solubility in mixed solvent systems if solute- and system-specific solubility parameters were regressed from experimental data. Compilations of these type of solubility parameters have been tabulated by Barton (1983).

Summary

This chapter presented results of interpretation of experimental data to predict aromatic solute solubility in co-solvent/water systems. Seven aromatic solutes were selected for evaluation in order to represent different physical and chemical characteristics with respect to hydrophobicity, polarity, hydrogen bonding, and functional group substitution. Data for eighteen aromatic solute/co-solvent/water systems were evaluated, and it was shown that in general there was a semi-logarithmic increase in solute solubility with an increase in the volume fraction of co-solvent. This confirmed the trend predicted by the log-linear approach for estimating solute solubility in co-solvent/water systems. This approach was the most easily applied of the various thermodynamic techniques for estimating solubility. However, it requires that some solubility data be available, preferably solubility in pure water and solubility in 50% or 100% co-solvent. While aqueous solubility is commonly available for many aromatic solutes, relatively little information exists on solubility of aromatic compounds in various co-solvents. The log-linear solubility prediction was evaluated through knowledge of solute solubility in 100% water and measured or estimated solubility in 100% co-solvent. Solute solubility in 100% co-solvent was estimated according to the UNIFAC group contribution model where necessary. The log-linear prediction gave a bias of 95.7% where 100% represents perfect prediction, with an accuracy of 187% where 100% represents perfect estimation.

The UNIFAC group contribution model was used to estimate solute solubility in water and co-solvent/water mixtures. This approach was unique among the predictive techniques in that it does not require specific measurements in order to obtain correlation coefficients or other parameters. The UNIFAC procedure was used to predict infinite dilution activity coefficients, γ^{∞}, from which mole fraction or mass solubilities were estimated. The UNIFAC procedure employs a solution-of-groups concept in which infinite dilution activity coefficient is given from specification of mole fraction solvent composition and functional groups comprising the solute, co-solvent and water. This procedure predicted solute solubility in pure water and in 100% co-solvent within a factor of approximately two. These predictions comprised a range of solute solubilities spanning approximately six orders of magnitude. The bias of this group contribution approach for prediction of solute solubility in mixtures for the eighteen co-solvent/water systems was 65.4% with an accuracy of 321%.

An excess free energy approach was also evaluated for predicting solute solubility. This technique required use of the UNIFAC procedure to predict co-solvent/water interaction constants. This approach also required regression of experimental data to obtain a solute-solvent interaction parameter. The various solute-solvent interaction parameters were correlated with solute octanol/water partition coefficient, and this correlation was employed as part of the predictive procedure. It was found that the excess free energy model provided the best value of accuracy of 174%. However, this was achieved through use of a more cumbersome approach requiring experimental data and an empirical correlation. The excess free energy procedure may be useful for estimating solute solubility for solutes for which UNIFAC functional group surface and interaction parameters are unavailable.

A molecular surface area technique was shown to be able to predict solute solubility with a accuracy of about 250% for the one solute/co-solvent/water system for which appropriate surface area and interfacial energy terms were available. The use of standard solubility parameters and regular solution theory was inappropriate for predicting solute solubility in the co-solvent/water systems, although a form of the regular solution equation could be used to empirically correlate solubility data through regression of experimental results to obtain solute and solvent-specific solubility parameters.

Chapter 5

EFFECT OF ORGANIC SOLVENT ON SORPTION OF AROMATIC SOLUTES ONTO SOILS

Introduction

This chapter outlines an approach to investigate procedures for predicting sorption of certain types of aromatic hydrocarbons onto soils from an aqueous phase containing polar organic solvent. The work described in this chapter is comprised of both data base and theoretical developments. The theoretical developments are used for experimental design and data interpretation. The motivation for this work is derived from the need to understand pollutant sorption onto soils for systems containing appreciable concentration of polar solvent in the aqueous phase. The work is applicable to understanding near-source contaminant transport in the event of spill or discharge to soil systems of organic wastes containing water-soluble solvents.

The purpose of this work is to improve understanding of the manner in which organic chemicals may move through soil or sediments. It is known that hydrophobic organic solutes can be retarded in movement through soil relative to the bulk movement of water, and it is also known that sorption of hydrophobic organic solutes onto soil can play an important role in the retardation of the transport process. This chapter includes a discussion of these phenomena. This discussion is then used to develop a model to describe the sorption of aromatic solutes onto soil for systems containing miscible, polar organic solvent in the aqueous phase. The chapter begins with a synthesis of information regarding sorption of aromatic hydrocarbons onto soil. This includes an evaluation of procedures that enable estimation of sorption characteristics for aromatic hydrocarbons from pure water systems, and then these procedures are extended in conjunction with results presented in Chapter 4 to those systems that contain organic solvent/water mixtures. The procedures incorporate several physico-chemical properties of the system including: soil organic carbon content, solute solubility in the solvent/water mixture, and other chemical characteristics of the aromatic hydrocarbons. The discussion of sorption phenomena is followed by a description of an experimental methodology and results of laboratory tests to observe sorption of organic solutes onto soils from systems containing various proportions of polar solvents. This information is then used to assess the validity of the sorption model.

Sorption of Aromatic Solutes onto Soils

At present there is much interest in evaluating the nature and extent of groundwater contamination from toxic/hazardous organic pollutants. Contamination of groundwater with synthetic organic materials presents major environmental problems in many areas of the United States and in other industrialized nations as well. Reports prepared by the U.S. Environmental Protection Agency (EPA) and the Council on Environmental Quality (CEQ) describe the magnitude of waste disposal practices in the U.S. and their effects on groundwater quality. Data presented (EPA, 1977, CEQ, 1980) indicate that thirty to fifty thousand waste disposal sites in the U.S. may contain hazardous materials. Although the extent of contamination is unknown, groundwater systems close to many of these sites are being slowly degraded and often the contamination involves the presence of synthetic organic materials (EPA, 1980).

Once groundwater has been contaminated, little can be done to reverse the damage. Frequently the only remedies for groundwater contamination problems involve extensive pumping or removal of soil, both of which are expensive and/or impractical propositions. In order to minimize the impact of man's activity on water quality, factors related to prevention and contamination need to be better understood. In this study, procedures are developed and evaluated that enable prediction of sorption characteristics for organic solutes onto soils from an aqueous phase that contains polar solvent. Organic solutes investigated in this study range from a nonpolar polycyclic aromatic hydrocarbon to polar, substituted aromatic compounds. Because of the hydrophobic nature of some of these compounds, sorption is important in determining the fate of these type of organic pollutants in natural water systems, and especially in subsurface systems.

Aqueous concentrations of hydrophobic organic solutes in natural water systems are highly dependent on sorptive/desorptive equilibria with sorbent present in the system. In subsurface systems, liquid to solid phase partitioning can play a significant role in the retardation of the transport of organic solutes (Fu et al. 1983). Sorption may also be involved in pollutant degradation via chemical reaction or biological degradation through attached growth biofilms (McCarty et al. 1981). Thus, understanding the fate of organic solutes in the subsurface environment greatly depends on understanding several aspects of the sorption process.

The Freundlich sorption model has been found to be useful for describing sorption characteristics of organic solutes in water/sediment and water/soil systems (Means et al. 1979, Karickhoff et al. 1979). The Freundlich sorption isotherm can be expressed as

$$\frac{S}{M} = K\ C_e^{1/n} \qquad (5\text{-}1)$$

where

S = total mass of solute sorbed [mg]

M = mass of solids [g or kg]

C_e = equilibrium concentration in the liquid phase [mg/l]

K = partition coefficient [l/g or l/kg]

K and 1/n are empirical constants which are characteristic of the solute and solids. If the sorption data are plotted on logarithmic scales with equilibrium concentration, C_e, on the abscissa and sorption capacity, S/M, on the ordinate, then according to Equation 5-1, K is the intercept of the sorption isotherm plot at C = 1 and 1/n is the slope of the isotherm. K is the measure of the strength of sorption, or sorption capacity, while 1/n is an indicator of sorption intensity. It is conventional to express C in units of mass per volume and S as mass sorbed per mass of dry soil. The units on K are usually given as l/kg or ml/g.

Many laboratory studies on organic solute sorption onto soils, sediments, and suspended solids have found that a linear sorption isotherm, e.g. 1/n = 1 in Equation 5-1, is useful in describing hydrophobic organic solute sorption onto these materials (Hamaker and Thompson, 1972; Karickhoff et al. 1979). Hamaker and Thompson (1972) summarized available soil Freundlich sorption isotherm data for a variety of chemicals, and the results show that the exponent 1/n varied from 0.7 to 1.0. Karickhoff et al. (1979) found that the sorption isotherms for various polycyclic aromatic hydrocarbon (PAH) compounds on pond and river sediments were linear (1/n = 1) over a range of aqueous phase concentrations up to about one half the compound's solubility in water. Rogers et al. (1980) performed sorption and desorption studies with benzene at concentration less than 1 mg/l with four soils and obtained sorption isotherms with 1/n values ranging from 0.9 to 1.1. Schwarzenbach and Westall (1981) have reported that a linear sorption isotherm can be used to describe sorption of non-polar organic solutes by natural sediments. These experimental results support the concept that a linear sorption isotherm is appropriate for describing sorption of a relatively hydrophobic organic solute on soil/sediment at low to moderate equilibrium concentration with respect to solute solubility.

Schwarzenbach and Westall (1981) and Karickhoff et al. (1979) found that non-polar organic compounds sorbed independently on soil through the linear portion of their respective isotherms when studied in a mixture at low to moderate concentration relative to compound solubility. Thus, in groundwater contamination problems involving a mixture of sorbable, non-polar, organic solutes at low concentration, it may be reasonable to expect that each species will sorb independently depending on physico-chemical properties of the solute. Thus sorption is expected to have significant retardation effect on transport of strongly sorbing organic solutes. The large degree to which transport of strongly sorbing contaminants can be retarded has been illustrated by Pickens and Lennox (1976) who simulated numerically the movement of a sorbing solute for a range of partition coefficients in simple two-dimensional groundwater systems.

It is known that organic solutes can be retarded in movement through soil relative to the bulk movement of water. For the case of hydrophobic organic solutes, predictive procedures have been developed which correlate a linear soil sorption partition coefficient with soil organic carbon content and physical and chemical properties of the solute. Notable among these approaches are procedures in which the organic solute sorption partition coefficient is related to the solute octanol-water partition coefficient, (K_{ow}). The linear sorption isotherm approach has been used successfully to describe sorption of hydrophobic organic solutes from an aqueous phase containing relatively low concentration of organic compounds (Karickhoff et al. 1979; Schwarzenbach and Westall, 1981; Means et al. 1980; Chiou et al. 1979). However, except for ongoing work at the University of Florida (Nkedi-Kizza et al. 1984; Woodburn et al. 1985), no studies have been reported in which the primary objective was to investigate sorption of relatively hydrophobic organic solutes from an aqueous phase containing high concentration of polar organic solvent.

Understanding sorption of organic solutes onto soil from an aqueous phase containing polar solvent is important for the purpose of evaluating pollutant transport for hazardous organic materials released to soil and groundwater systems as a result of accidental spill or improper/inadequate disposal. In these instances, the release of the hazardous materials may commonly be accompanied by the release of organic solvents, and these solvents may exert a strong influence on near-source transport. As discussed in the previous chapter, the presence of miscible organic solvent in the aqueous phase can significantly enhance organic solute solubility and thus reduce sorption characteristics. This is because the sorptive behavior of an organic solute can be related to solute properties, particularly solute solubility or solute octanol-water partition coefficient. Since organic solute sorption onto soils and sediments can be inversely correlated with the organic solute solubility (Means et al. 1980), it is expected that organic solute sorptive behavior may be altered significantly owing to the effect of miscible organic solvent on solute solubility enhancement. The following section outlines an approach to explain these phenomena by encompassing the relationships between organic solute sorptive behavior, soil and sediment properties, and organic solute solubility. The development focuses on mechanisms which may impact solubility and sorption, and this is used to describe a model to predict organic sorption in miscible organic solvent/water systems.

Sorption and Soil Organic Carbon Content

It is known that soils with higher organic material exhibit greater sorption capacities for hydrophobic organic compounds. The relative importance of the organic carbon content of a soil or sediment in the sorption of organic solutes has been well documented (Karickhoff et al. 1979; Karickhoff, 1981; Schwarzenbach and Westall, 1981; Rogers et al. 1980; Lambert et al. 1965). The difference in sorptive behavior between different types of soils and sediments may be accounted for by normalizing the partition coefficient on the basis of organic carbon content of the sorbent (Lambert et al. 1965).

The role of soil organic matter in the sorption of uncharged organic solutes has been studied extensively and it has been found that the organic matter in soil/sediments is primarily responsible for sorption (Karickhoff, 1981). In studies with hydrophobic organic solutes at low loadings, a linear correlation is often observed between solute partition coefficient (K_p) and soil/sediment organic carbon content (OC). The linear dependence of partition coefficient on organic carbon content can be expressed as

$$K_p = K_{oc}\,OC \tag{5-2}$$

where OC is the fraction organic carbon content, and K_{oc} is the normalized organic carbon partition coefficient. Hamaker and Thompson (1972) suggested that K_{oc} is highly soil or sediment independent and is constant for a particular organic solute. A similar conclusion is made by Karickhoff (1984), in his review of sorption of uncharged organic solutes of limited solubility ($< 10^{-3}$ M) that are not susceptible to special interactions with soil organic carbon. For a soil/sediment with a particular particle size distribution (by weight) having various organic carbon contents, the partition coefficient can be expressed as the weighted arithmetic mean of the separate contributions to sorptive behavior (Karickhoff et al. 1979).

Karickhoff (1984), following Mackay (1979), explains that sorption equilibrium may be defined as the state in which sorbate fugacities are the same in the aqueous and sorbed phases. For systems in which sorption to organic matter dominates over sorption to mineral matter, the organic carbon normalized partition coefficient may be envisioned as being proportional to the ratio of the compound's activity coefficient, γ, in the aqueous phase (w) and the organic carbon phase (oc)

$$K_{oc} \propto \frac{\gamma_w}{\gamma_{oc}} \tag{5-3}$$

in which the proportionality constant contains the reference state fugacities and appropriate unit conversion factors. Further, Karickhoff (1984) explains that activity coefficients "contrast" interactions of the solute in a given phase with the cohesive interactions in the reference state (i.e. pure liquid or subcooled liquid). Thus it may be expected for relatively hydrophobic organic solutes that γ_w be highly variable, as are variations in aqueous solubility;

while γ_{oc}, reflecting cohesive interactions in the organic carbon phase, should be similar to that for the reference state and therefore much less variable. Hence, K_{oc} should be dominated by variations in γ_w, and as a first approximation

$$K_{oc} \propto \gamma_w \tag{5-4}$$

K_{oc} and Octanol/Water Partition Coefficient

The octanol/water partition coefficient, K_{ow}, like K_{oc} describes the partitioning of a solute between an aqueous phase and a relatively immiscible hydrophobic phase. For a solute in equilibrium with octanol and water, the fugacity is the same in each phase, and K_{ow} is given as the ratio of the mass concentration in each phase

$$K_{ow} = \frac{C_{oct}}{C_w} \propto \frac{\gamma_w}{\gamma_{oct}} \tag{5-5}$$

where the proportionality with activity in each phase entails the ratio of the molar volume of water to octanol, and where the same standard state is chosen for the solute in each phase (i.e. pure liquid or subcooled liquid).

Since K_{oc} and K_{ow} both describe organic solute partitioning between water and a hydrophobic organic phase, it may be expected that these parameters would be related

$$K_{ow} \propto K_{oc} \tag{5-6}$$

The concept embodied in Equation 5-6 entails correlation of a partition coefficient for a given solvent/water system with that for a reference solvent/water system. This has been termed linear free energy relationships, and Leo and Hansch (1971) have shown that octanol is a particularly good choice of reference solvent. Octanol/water partition coefficient data are available for a large number of compounds. Current tabulations may be obtained from Corwin Hansch as part of the MEDCHEM project at Pomona College, California, as well as from various handbooks and research documents (Lyman et al. 1983; Hansch and Leo, 1979). In addition, various semi-empirical approaches are available from which K_{ow} may be estimated from solute physical, chemical or structural characteristics (Lyman et al. 1982). Reported values of K_{ow} for the organic solutes employed in this investigation are shown in Table 5-1.

Linear free energy correlations with K_{ow} have been used to describe aqueous solubility (Chiou et al. 1982), bioaccumulation (Chiou et al. 1977; Neely and Mackay, 1982), aromatic solute partitioning between immiscible solvent and water (Campbell et al. 1983), and sorption of organics onto soils (Lambert, 1967; Dzombak and Luthy, 1984).

Various empirical expressions have been developed to describe the relationship between K_p and K_{ow} (Briggs, 1973; Karickhoff etal. 1979; Means et al. 1980; Karickhoff, 1984). These investigators have reported excellent correlation between K_{oc} and K_{ow} for hydrophobic solute sorption, with a linear regression equation usually given in the form

$$\log K_{oc} = a \log K_{ow} + b \tag{5-7}$$

where a and b are regression coefficients. Several examples of these equations are described below.

Karickhoff et al. (1979) found a linear relationship between K_{oc} and K_{ow} from linear regression analysis of sorption data for ten compounds, including eight aromatic solutes:

$$K_{oc} = 0.63\ K_{ow} \qquad r^2 = 0.96 \tag{5-8}$$

A linear regression of various sorption data gave a correlation between log K_{oc} and log K_{ow} for forty-seven organic solutes, including twenty-two hydrocarbons, for which Karickhoff (1981) summarized as

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346 \qquad r^2 = 0.997 \tag{5-9}$$

Means et al. (1980) verified a linear relationship between K_{oc} and K_{ow} for a variety of nonpolar compounds including various polycyclic aromatic

Table 5-1: Organic Solute Octanol/Water Partition Coefficients*

Compound	log K_{ow}
Naphthalene	3.35
Naphthol	2.71
Quinoline	2.04
3,5-Dichloroaniline	2.59
Aniline	0.90
Phenanthrene	4.46
o-Xylene	3.20

* After Hansch and Leo (1979)

hydrocarbons. Based on sorption studies for twenty-two compounds on various soils and sediments, the relationship between K_{oc} and K_{ow} was given as

$$\log K_{oc} = \log K_{ow} - 0.317 \qquad r^2 = 0.98 \tag{5-10}$$

Schwarzenbach and Westall (1981) investigated the sorption of halogenated alkanes and benzenes, and for low concentrations they found that the partitioning between water and sediment could be described as

$$\log K_{oc} = 0.72 \log K_{ow} + 0.89 \qquad r^2 = 0.95 \tag{5-11}$$

Karickhoff (1984) concluded from these and other results that the correlation between K_{oc} and K_{ow} was "a somewhat divergent group of relationships". This was attributed to various factors including hydrophilic contribution to sorption, as well as kinetic or steric effects. It was suggested that hydrophilic effects would be evident for solutes containing polar functional groups which tend to be those with values of log $K_{ow} < 3$, while kinetic or steric effects would be more pronounced for those compounds having values of log $K_{ow} > 5$.

K_{oc} and Solute Solubility

As explained in Chapter 2, organic solute solubility in water can be realted to the solute's infinite dilution activity coefficient, γ_2^{∞}. For hydrophobic liquid solutes having sufficiently large values of γ_2^{∞}, mole fraction solute solubility can be expressed as the reciprocal of the activity coefficient (Equation 2-39). For hydrophobic solids, a crystal energy term must be taken into account, and the solute solubility can be expressed as Equation 2-31. If entropy of fusion, ΔS_f, is substituted for heat of fusion, ΔH_f, by using Equation 2-33, then the relationship between activity and mole fraction solubility can be expressed as

$$\log \gamma_2 = - \log X - \frac{\Delta S_f (T_m - T)}{2.303 \; RT} \qquad (5\text{-}12)$$

in which T_m is the solute melting point in °K, T is the system temperature in °K, and R is the gas constant. For hydrophobic liquid solutes, the system temperature is greater than the melting temperature, and T is set equal to T_m and the crystal term vanishes. Yalkowsky and Valvani (1980) have reviewed ΔS_f data for "rigid" organic solutes which are solids at 25 °C, and it was found that ΔS_f is not highly variable and is in the range of 12 - 15 cal/mole °K. "Rigid" solutes include cyclic compounds (alphatic or aromatic) and molecules with less than five atoms in a flexible chain (Yalkowsky and Valvani, 1980). Nonrigid molecules typically melt at much lower temperatures than rigid molecules for molecules of similar molecular weight, and thus are frequently liquid at room temperature. It has been long recognized by chemical thermodynamicists that a value of ΔS_f is in the range of 13 cal/mole °K for solid organic compounds (Prausnitz, 1969).

Equation 5-4 suggests that K_{oc} should be proportional to γ_2. Hence by combining Equation 5-4 and 5-12, an empirical equation of the following type may be expected to fit observed sorption data

$$\log K_{oc} = - \alpha \log X - \frac{\Delta S_f}{2.303 \; RT} (T_m - T) + \beta \qquad (5\text{-}13)$$

in which α and β are regression-fitted parameters. Karickhoff (1981) performed an evaluation of Equation 5-13 for condensed ring aromatic compounds using K_{oc} data of Hassett et al. (1980) for benzene and polycyclic aromatic hydrocarbon (PAH) compounds, with ΔS_f assumed to be 13.0 cal/mole °K and system temperature T at 298 °K (25 °C). The empirical equation was given as

$$\log K_{oc} = 0.921 \log X - 0.00953 (T_m - 298) - 1.405 \qquad (5\text{-}14)$$

This equation was evaluated for a variety of organic solutes (triazines, carbamates, organophosphates, and chlorinated hydrocarbons), and was found to estimate K_{oc} usually within a factor of 2 to 3 of measured values (Karickhoff, 1984). It was found that Equation 5-13 worked well for low molecular weight compounds but tended to overestimate sorption of highly chlorinated, high molecular weight compounds. It was concluded that α values for these type of compounds may be in the range of 0.7 to 0.8 which is considerably less than that for polycyclic aromatic hydrocarbons.

Karickhoff (1984) evaluated the sorption literature values for forty-seven organic compounds including PAH and chlorinated hydrocarbons, triazines, carbamates, organophosphates and phenylureas and found that the α value in Equation 5-13 was 0.83 and the β value was -0.93

$$\log K_{oc} = -0.83 \log X - 0.01 (T_m - 298) - 0.93 \qquad (5\text{-}15)$$

Solvent Effect on Solute Sorption

Equations 5-2 through 5-6 and Equation 5-13 may be summarized as follows. Linear partition coefficients are often observed for hydrophobic organic solute sorption onto soil or sediments. The sorption partition coefficient may be normalized for soils and sediments on the basis of fraction organic carbon, and normalized for various solutes on the basis of octanol/water partition coefficient or aqueous solubility. Hence for a given soil or sediment, organic solute sorption is inversely proportional to aqueous solubility. The following explains a theoretical approach for predicting the observed effect of miscible organic solvent in the aqueous phase on organic solute sorption onto soil or sediment. This approach is based on the linkage between K_{oc} and aqueous solubility, and the effect of solvent on solubility.

It has been demonstrated in Chapter 4 that organic solute solubility in a solvent/water mixture generally increases semi-logarithmically with increase of volume fraction of solvent. Using the simple log-linear solubility model, the mole fraction solubility of the solute in the solvent/water mixture can be expressed as

$$\log X_m = \log X_w + \sigma z \qquad (5\text{-}16)$$

where X is the mole fraction solubility of the solute, and subscripts m and w represent solvent/water mixture and water, z is the volume fraction of solvent, and σ is the regression constant obtained from experimental mole fraction solubility data.

As discussed in the previous section, the sorption partition coefficient, K_p for hydrophobic organic solutes can be normalized on the basis of organic carbon content of the soil. K_{oc} can be expressed as the ratio of solute activity coefficients in the aqueous phase and organic matter phase (Equation 5-3), for which the activity coefficient in the aqueous phase should be dominant. Aqueous phase activity coefficient may be given by Equation 5-12, and this leads directly to Equation 5-13.

For a solvent/water mixture, the mole fraction solubility can be expressed by Equation 5-16. By combining Equations 5-13 and 5-16, the solute sorption coefficient K_{oc} can be expressed in terms of solute solubility

$$\log K_{oc} = -\alpha \log X_w - \alpha \sigma z - \frac{\Delta S_f}{2.3RT}(T_m - T) + \beta \qquad (5\text{-}17)$$

Rearranging Equation 5-17 gives

$$\log K_{oc} = [-\alpha \log X_w - \frac{\Delta S_f}{2.3RT}(T_m - T) + \beta] - \alpha \sigma z \qquad (5\text{-}18)$$

The first three terms in the right hand side of Equation 5-18 represent the solute K_{oc} in pure water, denoted as $K_{oc,w}$, therefore

$$\log K_{oc} = \log K_{oc,w} - \alpha \sigma z \qquad (5\text{-}19)$$

Substituting into Equation 5-2 gives

$$\log \frac{K_{oc}}{K_{oc,w}} = \log \frac{K_p}{K_{p,w}} = -\alpha \sigma z \qquad (5\text{-}20)$$

It is important to recognize that the basis of derivation of Equation 5-20 depended on the relationship between mole fraction solubility and K_{oc}. The units in K_{oc} must therefore be consistent with the expression of solubility in terms of mole fraction. This is not strictly necessary for the case of comparison of different values of log $K_{oc,w}$, as in Equation 5-13, where the partition coefficient may be employed with customary units of l/kg. In this case the number of moles per liter is constant for dilute aqueous systems, i.e. 55.3 mole/l, and this value becomes incorporated in the regression constant β in Equation 5-13. However, for the case of solvent/water mixtures, the total number of moles per liter is not constant and the partition coefficient must be expressed in units of mole/kg. Thus, in order to use Equation 5-20, the ratio of the experimentally determined sorption coefficients must be expressed on the basis of total moles per unit mass of soil

$$\log \frac{K_p \left(\frac{V_{water}}{q_{water}} + \frac{V_{solvent}}{q_{solvent}} \right)}{K_{p,w}\ (55.3)} = -\alpha \sigma Z \qquad (5\text{-}21)$$

where V refers to the solute-free volume of water or solvent in the mixtures, and q represents the molar volume of water or solvent.

Equation 5-20 shows that K_p for a solvent/water mixture is expected to decrease semi-logarithmically with increase of solvent volume fraction. The semi-logarithmic relationship predicted by Equation 5-20 can be shown on a semi-logarithmic plot with volume fraction solvent on the abscissa and K_p (mole/kg) on the ordinate. The slope of this plot represents the combined effect of both α and σ. The σ term represents the effect of solvent on increase of solute solubility, while the α term relates to the dominance of γ_w in K_{oc} among various solutes. The α term should approach unity if the fugacity coefficient for solute in soil/sediment organic carbon is relatively independent of solute (Karickhoff, 1984), and if the soil organic carbon properties are independent of change in solution phase composition.

Soil sorption partition coefficient data are reported later in this chapter for various solutes in solvent/water systems. From these data it is possible to determine experimental values of the coefficient in Equation 5-20, $(\alpha\sigma)_{exp}$. Since σ is known from data presented in Chapter 4, it is possible to determine an explicit value for $(\alpha)_{exp}$. If $(\alpha)_{exp}$ is significantly less than unity, then the effect of solvent on decrease in sorption partition coefficient will not be as significant as the effect of solvent on increase of solute solubility. If $(\alpha)_{exp}$ approaches unity, then the effect of solvent on decrease of sorption partition coefficient is directly proportional to the effect of solvent on increase of solute solubility.

Organic Solute Sorption onto Soils in Solvent/Water Mixtures

Sorption isotherms for four aromatic solutes (naphthalene, naphthol, quinoline, and 3,5-dichloroaniline) were determined by batch tests. Two solvents (methanol and acetone) were used. Three soils (Hagerstown silt loam, Berkeley silt loam, and Tifton sand) were used as sorbents. This section describes the materials, reagents and analytical techniques used in the investigation.

Soils The soils used in this study were Hagerstown silt loam, Berkeley silt loam, and Tifton sand. Hagerstown silt loam was used as the principal soil, and was obtained from the Department of Agronomy Experimental Station, The Pennsylvania State University (University Park, PA). The Hagerstown silt loam was taken from within two feet of the ground surface. The Berkeley silt loam and Tifton sand were used for screening tests, and were obtained from the U.S. Department of Agriculture, Agricultural Research Center (Beltsville, MD). Prior to storage, the soils were air-dried and screened to pass a U.S. standard sieve No. 10 (2.0 mm). This procedure removed any grass and plant root. The physical characteristics of the soils are described in Appendix D.

Chemicals and Reagents Organic solvents used in this study included methylene chloride (CH_2Cl_2), methanol (CH_3OH), acetone (C_3H_6O), and acetonitrile (CH_3CN). These solvents were HPLC grade and were obtained from Fisher Scientific Company (Pittsburgh, PA). All organic solvents were filtered through 0.45 μm teflon filters and degassed prior to use.

Water was filtered, deionized, and purified by a carbon bed system supplied by Continental Water Corporation (El Paso, TX). This system passes tap water through a filter, resin ion exchange column, and then a carbon bed. Deionized water was then filtered through a 0.45 μm cellulose filter and degassed.

Chemical reagents were obtained from Fisher Scientific Co. and Aldrich Chemical Co. (Milwaukee, WI). Scintillation grade or certified grade naphthalene, naphthol, and 3,5-dichloroaniline, having purity of 99% or higher, were obtained as crystalline powder. Quinoline was obtained from Fisher Scientific Co. as certified grade, having purity higher than 99%. All chemical reagents were used as received. The name "naphthol" refers to the compound α-naphthol.

Glassware All glassware used in this study was carefully cleaned in order to minimize contamination. All glassware was first washed with soap and water; glassware was then soaked in a 1:1 nitric acid bath for twenty-four hours, followed by rinsing with deionized water, acetone, methanol, methylene chloride, and water, respectively. Following these procedures, the glassware was oven dried at 105 °C and covered with aluminum foil until used.

Experimental Instrumentation Solute analyses were performed with a high pressure liquid chromatography (HPLC) system made by Perkin-Elmer Corporation (Norwalk, CT). This system consists of a Series 3 liquid chromatograph and two detector units. A Perkin-Elmer model 204-S fluorescence detector equipped with variable excitation and emission wavelength setting was used for naphthalene and naphthol analysis. A

Perkin-Elmer model LC-15 ultraviolet (UV) detector with a fixed wavelength (254 nm) was used to measure quinoline and 3,5-dichloroaniline. Sorption batch tests were performed using a wrist action shaker (Model 74, Burrell Corp. Pittsburgh, PA). Centrifuging was performed using a IEC clinical centrifuge from International Equipment Co. (Needham Hts, MA).

A Hamilton (Reno, NV) Series 800 microliter syringe was used to inject samples of between 2 and 10 microliters into a Rheodyne (Berkeley, CA) Model 7105 injection valve fitted with a 175 μl sample loop. Either a 0.26 mm x 25 cm Perkin-Elmer PAH/10 column or a 0.46 mm x 25 cm Supelco (Bellefonte, PA) LC-PAH column was used to provide resolution for naphthalene and naphthol. A Supelco 0.46 mm x 15 cm LC-8 column provided resolution for quinoline and 3,5-dichloroaniline. Results were recorded on a compatible strip chart recorder, and results were determined using a planimeter (Kouffel & Esser Co. W. Germany).

Sorption Isotherm Tests

Sorption of organic solutes onto soils was investigated by batch tests with a solution phase comprised of 0.01 N $CaCl_2$ inert electrolyte. The electrolyte concentration was 0.01 equivalent per liter of solution, whether water or solvent/water mixtures. The electrolyte assisted in settling and separation of fine particles after the solute attained sorption equilibrium. Batch sorption shake tests were performed to obtain isotherm data. Sorption isotherms for a series of organic solutes were run with a variety of solvent/water ratios with a range of initial solute concentration. The solvent/water mixture was first prepared by adding solvent (methanol or acetone) to deionized water, and then degassed prior to adding a known quantity of solute and $CaCl_2$ into solution to make up the initial concentration. The solute and $CaCl_2$ were measured to 10^{-4} g.

The sorption tests involved equilibration at room temperature (23°C ± 2 °C) with different sets of samples having different values of initial solute concentration and various quantities of soil. The initial solute concentration was varied from set to set in order to obtain the complete sorption isotherm. The shake tests were performed with 50 ml glass centrifuge tubes fitted with teflon-lined screw caps. The amount of soil added to the centrifuge tubes was chosen to result in high and low equilibrium concentrations, and generally this included a range of 0.5 g to 40 g soil. In order to minimize volatilization loss, the experimental procedures consisted of placing a calculated amount of soil, weighed to 10^{-4} g, into a centrifuge tube, and then adding solution to fill the centrifuge tube without head space. The solution was measured to 0.1 ml via a calibrated burette. The centrifuge tube was then sealed with a teflon-lined septum and a screw cap with an access hole to allow for sample to be withdrawn through the septum. The centrifuge tubes were then covered with aluminum foil throughout the rest of the test in order to minimize photodegradation. One set of shake tests typically involved 16 samples, two of which were blanks and contained no soil. Each sample was replicated, and two or more tests with this number of samples were performed for each solute. Solute losses in blanks were less than 2% for those blanks in which the initial concentration was in the range of solute solubility in water.

After sample preparation, the sealed centrifuge tubes were transferred to a wrist-action shaker. Centrifuge tubes were shaken at room temperature for 24 hours to allow equilibrium to be achieved, after which the suspensions were centrifuged at 8000 rev/min for sixty minutes. Analyses were performed on liquid phase aliquots withdrawn from the upper portion of the centrifuge tube. The technique employed 2 to 10 microliter liquid aliquots withdrawn with a Hamilton series 800 microliter syringe. The sample was withdrawn from the centrifuge tube directly through the septum in order to minimize any loss during transfer. Analysis for the organic solutes was performed by high pressure liquid chromatography. The analytical program employed in this study was shown in Table 3-1. Results were recorded on a compatible strip chart recorder.

A planimeter (Kouffel & Esser Co. W. Germany) was used to quantify the resluts from HPLC analysis. This quantification was accomplished by measuring the area under the response curve for each sample. First the area corresponding to known standard concentrations (e.g. 1000 mg/l, 100 mg/l, 10 mg/l) were measured by performing at least triplicate injection of the standard. This was followed by obtaining the average area from several injections of sample. The total mass of the solute present in each sample was calculated by comparing the area under the injection curve with the area of the standard. Once the total mass of solute in the injected sample was determined, the concentration in the injected sample was calculated by taking the total mass of the solute divided by the volume of sample injected for the HPLC analysis.

Soil Organic Carbon Content

Carbon is the principal element of soil organic matter that can be readily measured quantitatively. Hence, estimation of soil organic matter is generally based on measuring soil organic carbon. Soil organic carbon includes (Allison,1965):

- Fresh plant and animal residues, capable of rapid decomposition and loss of identity with simultaneous release of nutrient elements;
- "Humus", which represents the bulk of resistant organic matter, having high sorptive capacity for cations and capable of improving soil structure; and
- Inert forms of nearly elemental carbon such as charcoal, coal or graphite.

In this study, organic carbon was determined by the Walkley-Black method (Allison, 1965). A soil sample containing 10 to 25 mg of organic-C was placed into a 500 ml wide-mouth Erlenmeyer flask, 10 ml of 1.0 N $K_2Cr_2O_7$ was added and the flask was swirled gently to disperse the soil in the solution. Then 20 ml of concentrated H_2SO_4 was added and swirled until soil and reagents were mixed, and then vigorously mixed for about one minute. The mixed solution was allowed to stand for 30 minutes and 200 ml of deionized water was added, and then the suspension was filtered. Three or four drops of a phenanthroline indicator were added to the solution, and the solution was titrated with 0.5 N $FeSO_4$. Titration results in a sharp end point with the color of the solution changing from blue to red. The amount of $FeSO_4$ used in titration was recorded. Blank determinations were made in the same manner to standardize the $K_2Cr_2O_7$ concentration.

The soil organic carbon content can be calculated according to the following equation, using a correction factor of f = 1.33 (Allison, 1965).

$$\text{Organic} - \text{C}\ [\%] = \frac{(\text{meq } K_2Cr_2O_7 - \text{meq } FeSO_4)\ (0.003)\ \ (100)\ (f)}{\text{g of dry soil}} \qquad (5\text{-}22)$$

where meq represents miliequivalent of the chemical used, and the constant 0.003 refers to the number of grams of carbon per miliequivalent carbon at an average oxidation state of zero. The correction factor, f, adjusts for the fact that soil organic carbon is typically at an average oxidation state slightly less than zero. The average organic carbon content of the Hagerstown silt loam was determined as 1.94%, while that for the Berkeley silt loam was 2.85%, and that for the Tifton sand was 0.50%. The reported percent organic carbon analysis represents the average of 14, 10 and 12 individual determinations for Hagerstown silt loam, Berkeley silt loam and Tifton sand respectively.

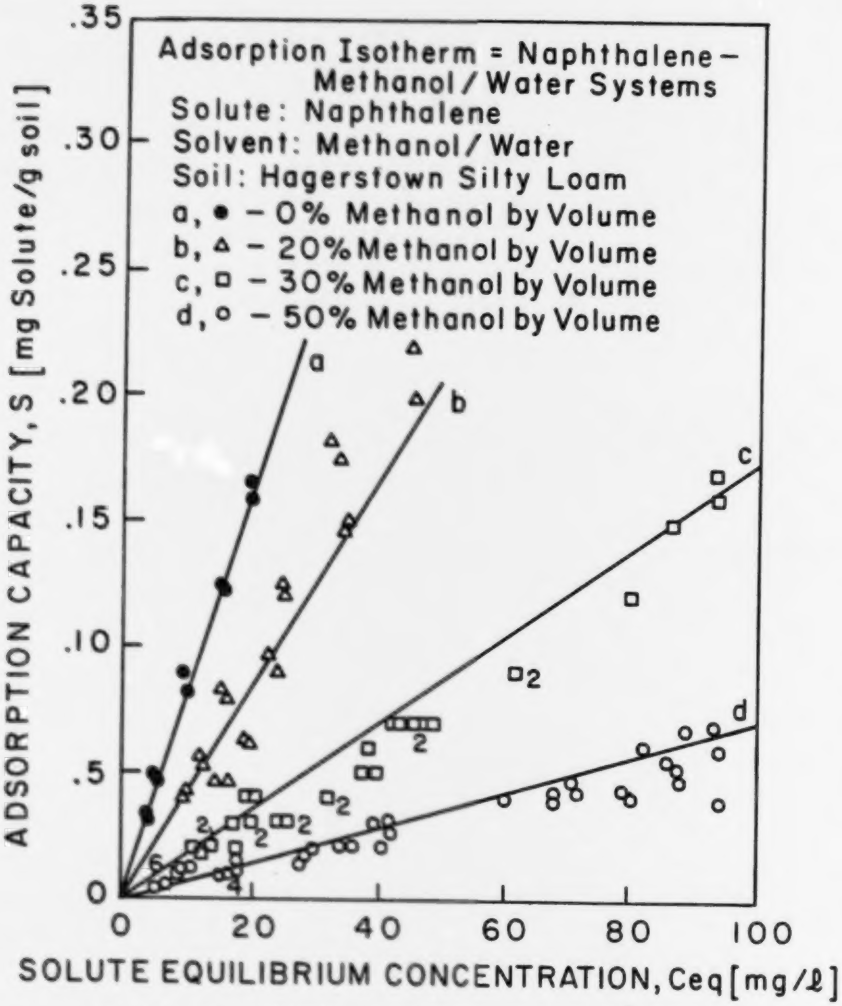
Solvent Effect on Solute Sorption

Sorption behavior of the organic solutes was evaluated with several solvent/water mixtures. This included investigation with four solutes (naphthalene, naphthol, quinoline, and 3,5-dichloroaniline) and two solvent/water mixtures (methanol/water, and acetone/water). The solvent/water mixtures ranged from 0% to 50% solvent by volume. Five systems were evaluated with Hagerstown silt loam as sorbent: naphthalene sorption with aqueous phase containing 0%, 20%, 30%, and 50% methanol; naphthalene sorption with aqueous phase containing 0%, 10%, 30%, 40%, and 50% acetone;

naphthol sorption with aqueous phase containing 0%, 20%, and 50% methanol; quinoline sorption with aqueous phase containing 0%, 20%, and 50% methanol; and 3,5-dichloroaniline sorption with the aqueous phase containing 0%, 20% and 50% methanol. The results of these five sets of sorption studies are shown in Figures 5-1 to Figure 5-5. The data shown in Figures 5-1 to 5-5 were obtained from tests in which sorbent and sorbate concentrations were varied in order that the complete sorption isotherm could be obtained. The results are characterized by linear sorption isotherms over the range of sorbate concentration. The sorption data were analyzed by linear-least-square curve fitting and the regression equations are shown in Figures 5-1 to 5-5. Except for the nonzero intercept observed with naphthol, the regression coefficients support the validity of a linear sorption isotherm model. In these figures, the units for K_p are given as l/kg, which is equal to 1000 times the slope of the linear regression relationships in which equilibrium concentration is given in units of mg/l and sorption capacity in units of mg/g. Figure 5-6 shows the variation in K_p for naphthalene sorption onto Hagerstown silt loam with methanol/water and acetone/water mixtures.

Naphthol sorption onto Hagerstown silt loam is shown in Figure 5-3. In this instance, a non-zero intercept is evident. This is attributed to naphthol sorbing through both hydrophobic and non-hydrophobic interactions with the soil. The non-hydrophobic sorption interactions are evident at low solute equilibrium concentrations. This is believed to be a result of the OH-group participating in strong site-specific interactions with the sorbent, such as through hydrogen bonding. Hassett et al. (1981) also have examined naphthol sorption onto various soils and sediments. Although these investigators chose to represent the sorption isotherms by the Freundlich equation in order to force the isotherm through the origin, their data with various samples suggest that the sorption of naphthol could be described by a linear isotherm with an intercept in the range of 0.7 mg/g. This intercept was evident for solute equilibrium concentrations as low as several mg/l or less. Hence, the sorption data of Hassett et al. (1981) agree with the results presented in Figure 5-3.

Figure 5-1: Naphthalene Sorption in Methanol/Water Mixtures



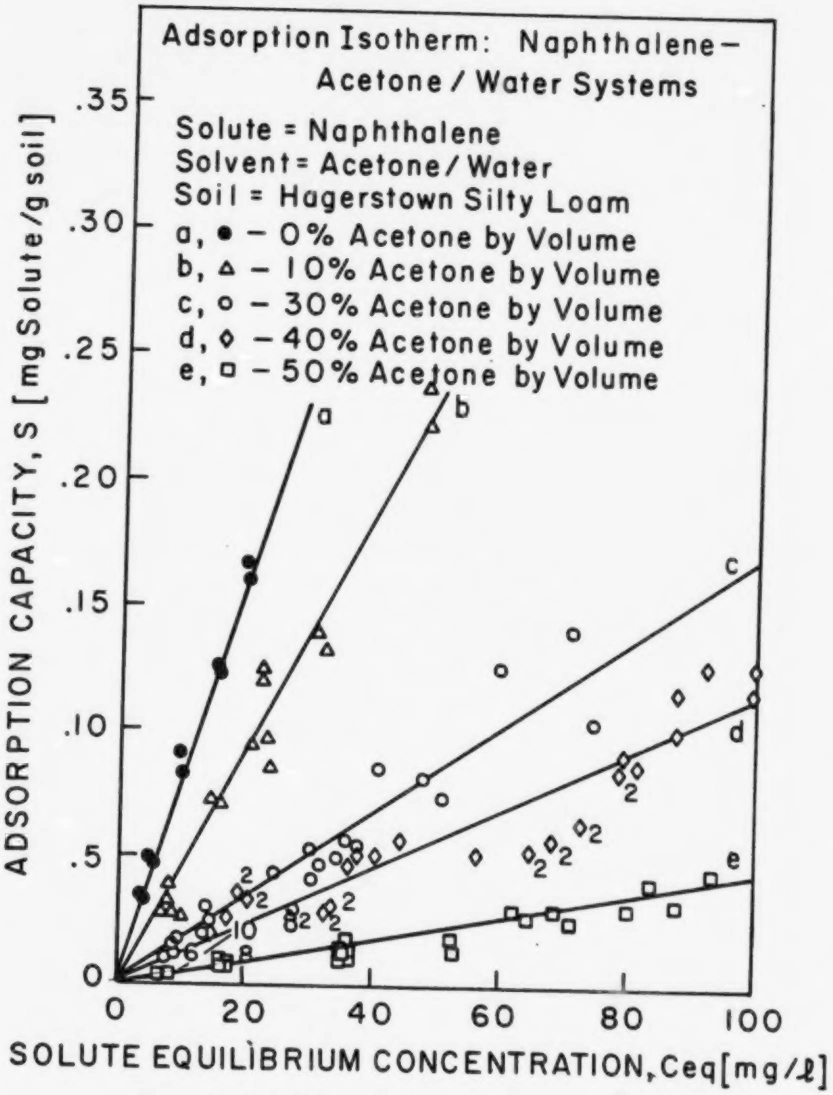
a. $S = 0.0020 + 0.0080\ Ceq \quad R^2 = 98.8\%$

b. $S = 0.0071 + 0.0040\ Ceq \quad R^2 = 88.3\%$

c. $S = 0.0105 + 0.0018\ Ceq \quad R^2 = 95.7\%$

d. $S = 0.0039 + 0.0007\ Ceq \quad R^2 = 87.4\%$

Figure 5-2: Naphthalene Sorption in Acetone/Water Mixtures



a. $S = 0.0020 + 0.0080\ Ceq \quad R^2 = 98.8\%$

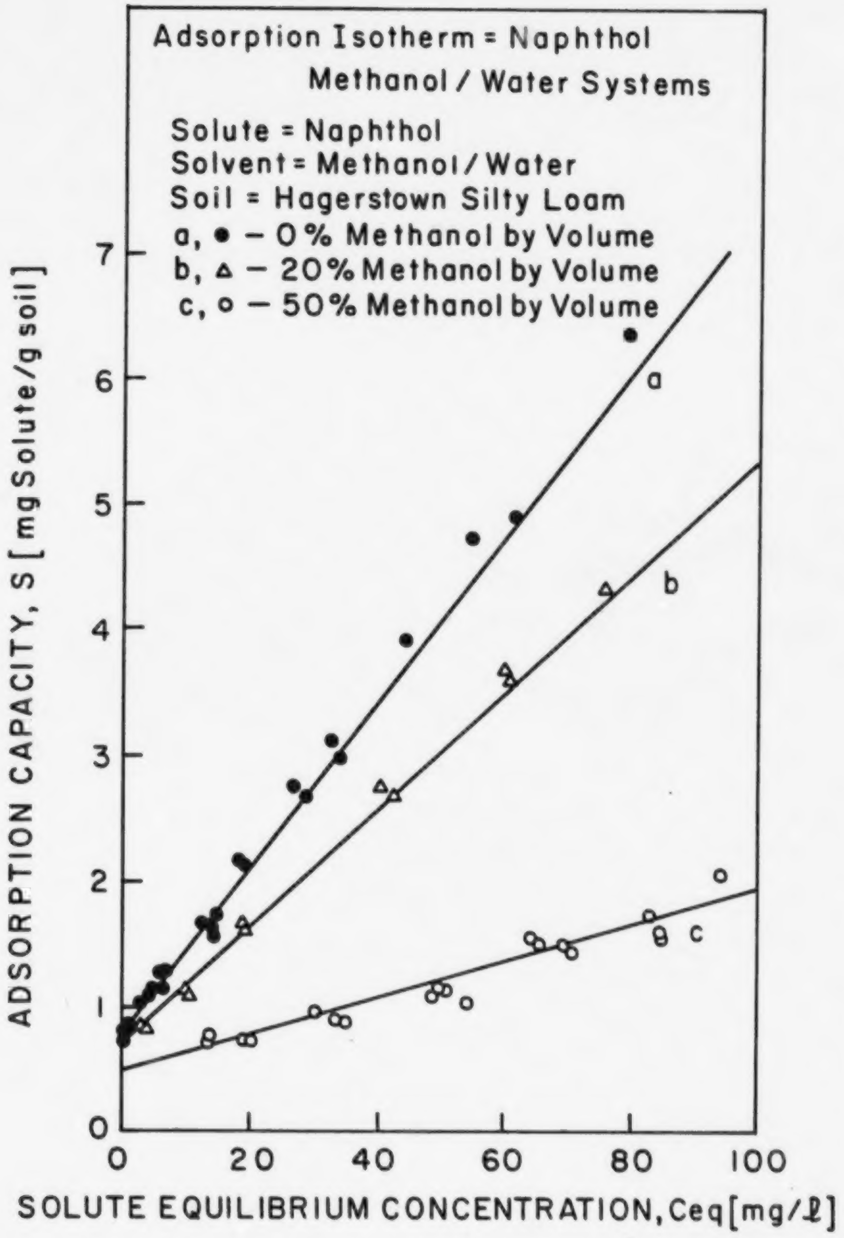
b. $S = -0.0205 + 0.0047\ Ceq \quad R^2 = 93.2\%$

c. $S = -0.0109 + 0.0018\ Ceq \quad R^2 = 84.7\%$

d. $S = 0.0012 + 0.0011\ Ceq \quad R^2 = 82.0\%$

e. $S = 0.0001 + 0.0005\ Ceq \quad R^2 = 93.2\%$

Figure 5-3: Naphthol Sorption in Methanol/Water Mixtures

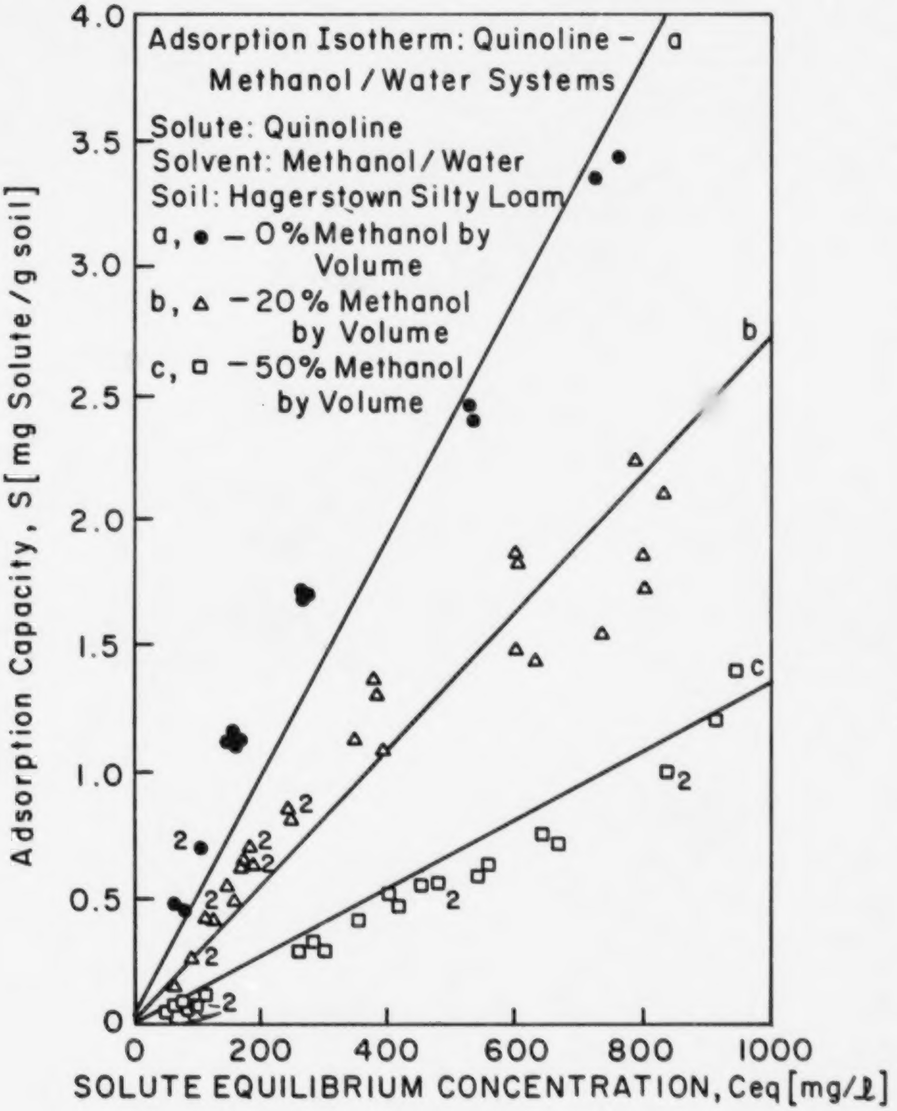


a. $S = 0.793 + 0.0074\ Ceq$ $R^2 = 96.7\%$

b. $S = 0.683 + 0.0047\ Ceq$ $R^2 = 98.3\%$

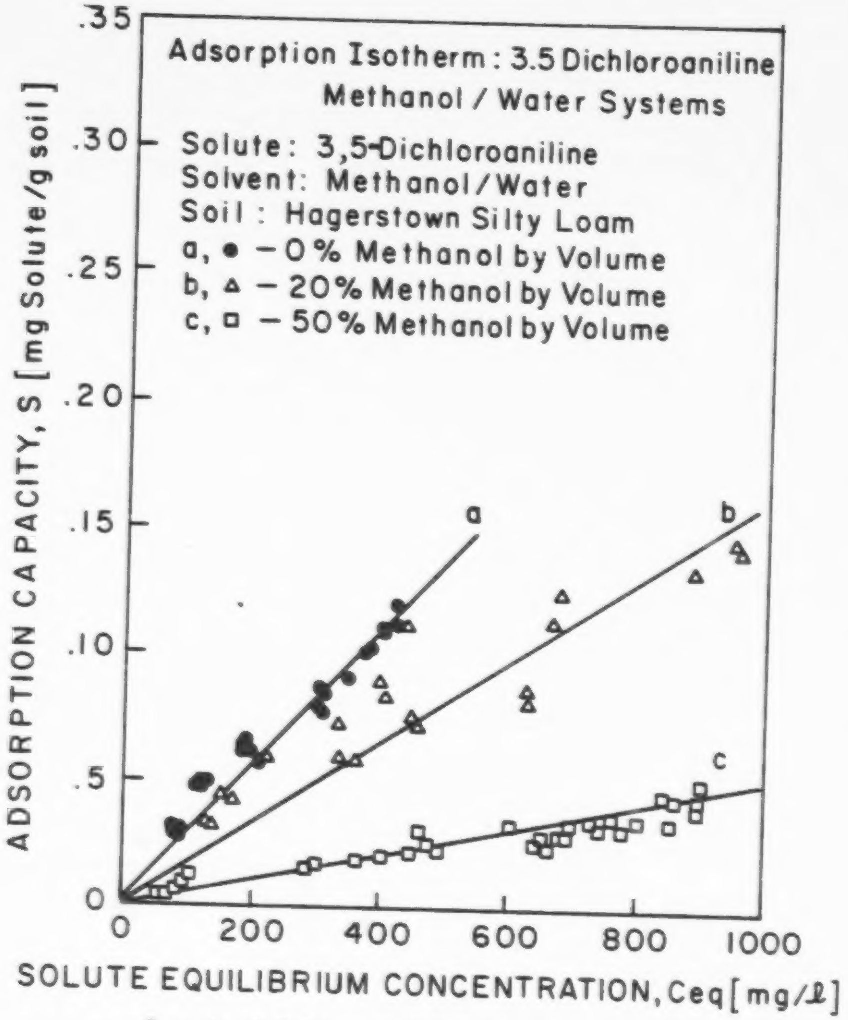
c. $S = 0.496 + 0.0014\ Ceq$ $R^2 = 83.3\%$

Figure 5-4: Quinoline Sorption in Methanol/Water Mixtures



a. $S = 0.352 + 0.0043\ Ceq$ $R^2 = 95.8\%$
b. $S = 0.147 + 0.0025\ Ceq$ $R^2 = 97.3\%$
c. $S = 0.111 + 0.0014\ Ceq$ $R^2 = 92.0\%$

Figure 5-5: 3,5-Dichloroaniline Sorption in Methanol/Water Mixtures

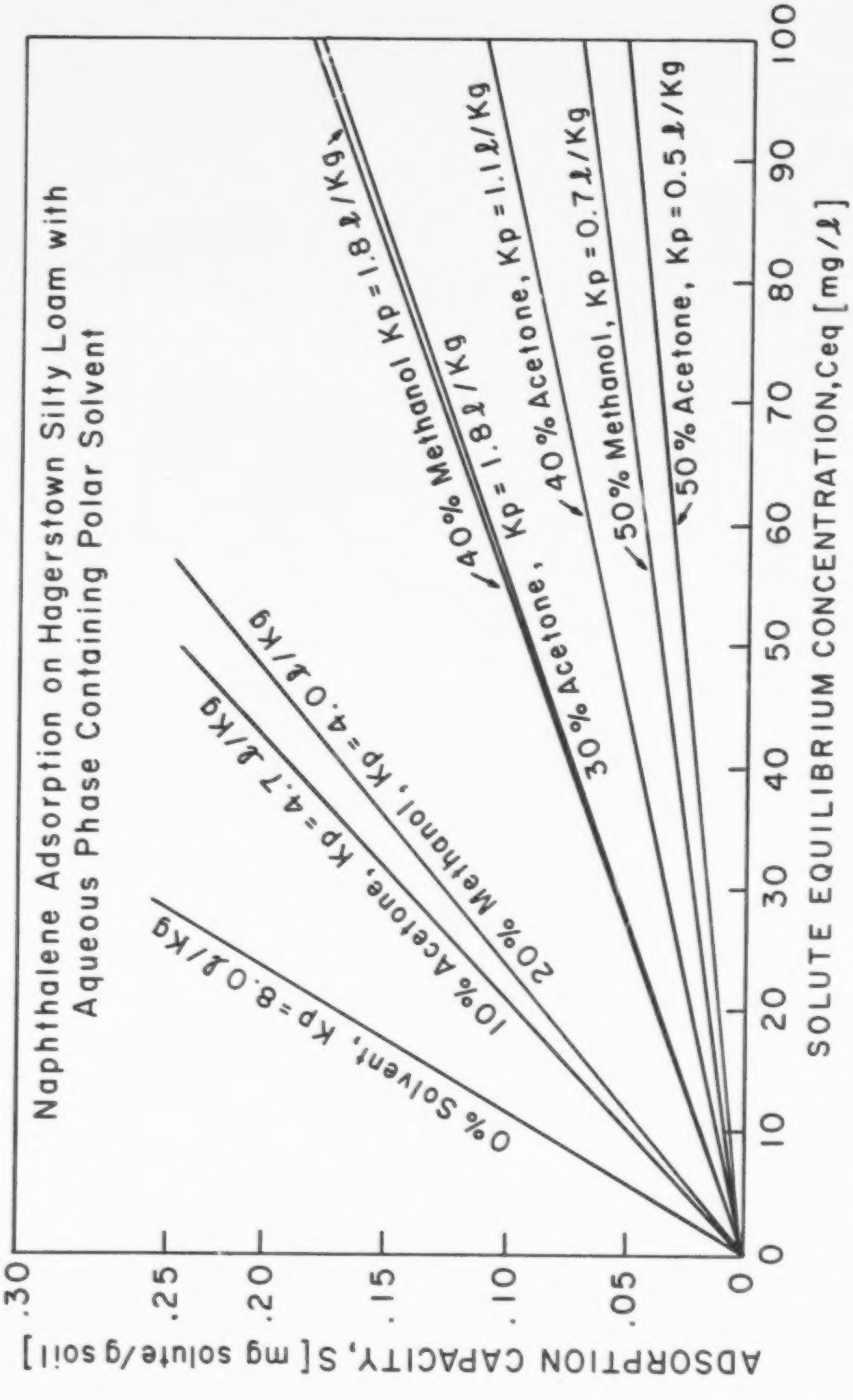


a. $S = 0.0921 + 0.0025\ Ceq \quad R = 96.5\%$

b. $S = 0.0151 + 0.0013\ Ceq \quad R = 90.4\%$

c. $S = 0.0094 + 0.0005\ Ceq \quad R = 93.8\%$

Figure 5-6: Naphthalene Sorption onto Hagerstown Silt Loam in Methanol/Water and Acetone/Water Mixtures



It is believed that the sorption of naphthol onto soil involves two phenomena, a strong site-specific interaction which accounts for the non-zero intercept of a linear sorption isotherm, and hydrophobic sorption interactions as described by the slope of the linear sorption isotherm. This description is possible because the strong site-specific interactions are satisfied at solute equilibrium concentrations of only several mg/l or less. It is the hydrophobic sorption interactions that are referred to in subsequent discussions on naphthol sorption, particularly with respect to the change in slope of K_p with increasing solvent content.

The results of organic solute sorption tests with Hagerstown silt loam with no organic solvent in the aqueous phase showed the following values of the sorption partition coefficients, K_p: naphthalene, 8.0 l/kg; naphthol, 7.4 l/kg; quinoline, 4.3 l/kg; and 3,5-dichloroaniline, 2.5 l/kg. The sorption partition coefficient for naphthalene sorption onto Berkeley silt loam was found to be 8.1 l/kg, and the sorption partition coefficient for naphthalene sorption onto Tifton sand was found to be 2.0 l/kg. These results show a solute dependence on the sorption partition coefficient. Linear-least-square regression of the K_{ow} and K_{oc} data was performed and the following equation described the sorption of the four solutes onto the soils with aqueous phase containing no solvent

$$\log K_{oc} = \log \frac{K_p}{OC} = 1.45 \log K_{ow} - 0.872 \qquad r^2 = 96.3\% \qquad (5\text{-}23)$$

This regression equation compares sorptive behavior for four aromatic solutes representing four different chemical types.

Methanol and acetone were used to evaluate the solvent effect on solute sorption characteristics on Hagerstown silt loam. Sorption isotherms with methanol/water mixtures were developed for four solutes (naphthalene, naphthol, quinoline, and 3,5-dichloroaniline), and sorption isotherms with acetone/water mixtures were developed for naphthalene. Figures 5-1 to 5-5 show sorption partition coefficients obtained at various volume fraction solvent for the five solute-solvent/water systems investigated in this study, where the results are plotted as sorption capacity [mg solute sorbed/g soil] versus equilibrium concentration [mg/l]. These results show that a linear sorption isotherm can be used to describe the sorption of organic solute onto soils with the various solvent/water mixtures. In these five systems, the sorption partition coefficient decreased significantly with increase in solvent volume content. For example, sorption partition coefficient for the naphthalene-methanol/water system is 8.0 l/kg for 0% methanol, 4.0 l/kg for 20% methanol, 1.8 l/kg for 40% methanol, and 0.5 l/kg for 50% methanol. Similar results were observed for the other four solvent/water systems as summarized in Table 5-2. Results in Table 5-2 show values of K_p expressed as both l/kg and mole/kg.

Figure 5-7 shows sorption partition coefficient (mole/kg) as a function of volume fraction of solvent for naphthalene sorption onto Hagerstown silt loam where the aqueous phase contains methanol or acetone as solvent. In general, the sorption partition coefficient is observed to decrease semi-logarithmically with increased solvent volume fraction. Similar phenomena were observed for naphthol, quinoline, and 3,5-dichloroaniline sorption onto Hagerstown silt loam in methanol/water systems, as illustrated in Figure 5-8.

The effect of solvent on organic solute sorption partitioning may be explained by invoking Equation 5-21. The σ value in this equation was obtained by regressing solute mole fraction solubility against volume fraction of solvent. The results of this analysis gave the following σ values: 3.79 for naphthalene-methanol/water systems; 5.14 for naphthalene-acetone/water systems; 3.01 for naphthol-methanol/water systems; 2.86 for quinoline-methanol/water systems, and 2.98 for 3,5-dichloroaniline-methanol/water systems. These values are slightly different than those which are obtained from regressing mass concentration solute solubility against volume fraction solvent as was shown in Figures 2-19 and 2-20. Equation 5-21 was examined using experimental sorption data for the seven systems investigated in this

Table 5-2: Sorption Partition Coefficients for Solvent/Water Mixtures

Hagerstown Silt Loam

Naphthalene-Methanol/Water

Methanol [% vol.]	K_p [l/kg]	K_p [mole/kg]
0	8.0	443
20	4.0	197
40	1.8	77.6
50	0.7	28.0

Naphthalene-Acetone/Water

Acetone [% vol.]	K_p [l/kg]	K_p [mole/kg]
0	8.0	443
10	4.7	241
30	1.8	77.1
40	1.1	42.6
50	0.5	17.3

Naphthol-Methanol/Water

Methanol [% vol.]	K_p [l/kg]	K_p [mole/kg]
0	7.4	410
20	4.7	232
50	1.4	56.1

Quinoline-Methanol/Water

Methanol [% vol.]	K_p [l/kg]	K_p [mole/kg]
0	4.3	238
20	2.5	123
50	1.4	56.1

3,5-Dichloroaniline-Methanol/Water

Methanol [% vol.]	K_p [l/kg]	K_p [mole/kg]
0	2.5	139
20	1.3	64.1
50	0.5	20.2

Berkeley Silt Loam

Naphthalene-Methanol/Water

Methanol [% vol.]	K_p [l/kg]	K_p [mole/kg]
0	8.5	471
20	4.4	217

Tifton Sand

Naphthalene-Methanol/Water

Methanol [% vol.]	K_p [l/kg]	K_p [mole/kg]
0	2.0	111
20	1.0	49.3

Figure 5-7: Solvent Effect on Sorption Partition Coefficient for Naphthalene-Methanol/Water Systems

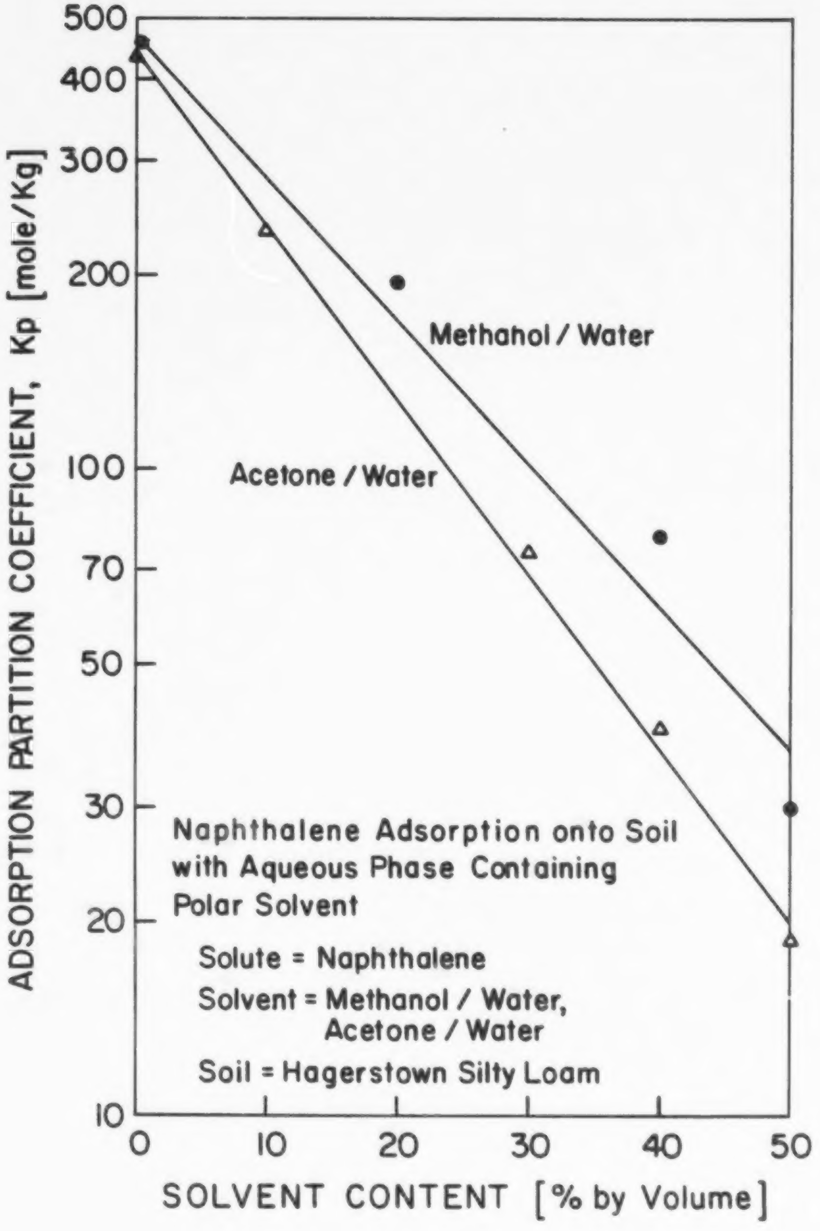
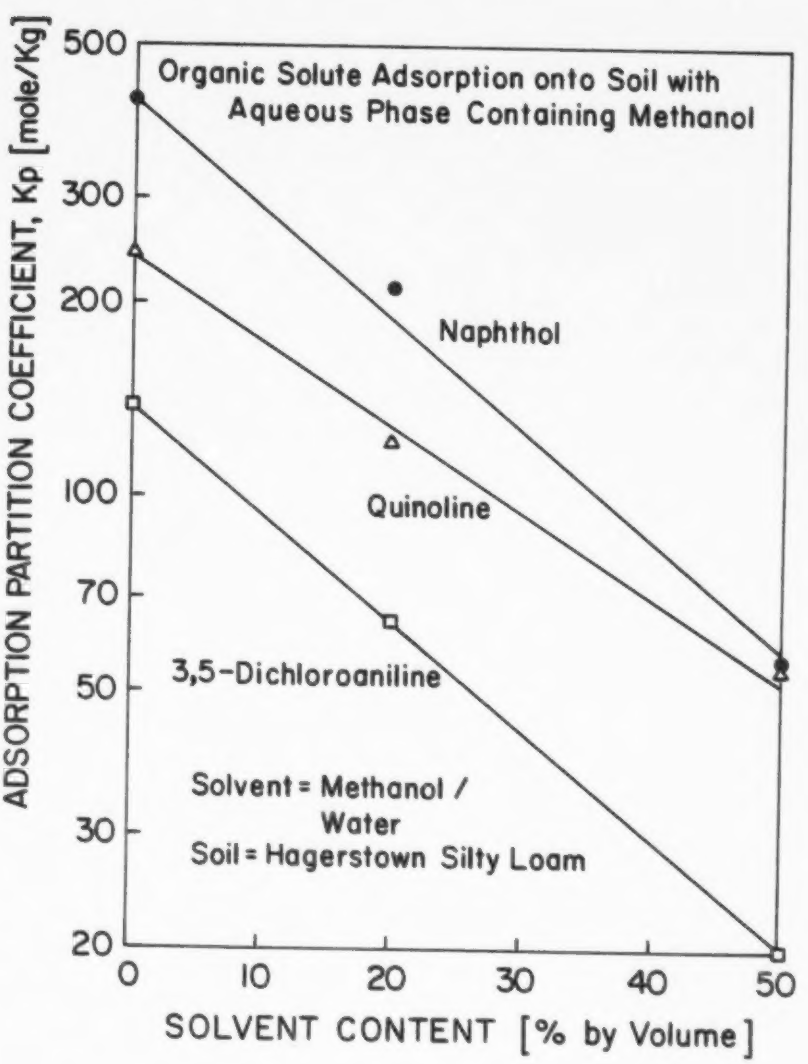


Figure 5-8: Solvent Effect on Solute Sorption Partition Coefficient for Methanol/Water Systems



study in conjunction with the respective σ values. The observed α values for these seven systems are presented in Table 5-3. This evaluation showed that the α values are in the range of 0.41 to 0.63. The average α value was 0.51 with a standard deviation of 0.060.

The range of observed α values are significantly less than unity, as well as uniformly less than a value of 0.92 as found by Karickhoff (1984) for condensed ring aromatic solute sorption onto soil/sediment for solvent-free systems. This implies, for a given solvent/water mixture, that the decrease of sorption partition coefficient is not as significant as increase in solute solubility. Further, the range of α values suggest that the logarithmic decrease in K_p is approximately half the logarithmic increase of solute solubility in a solvent/water mixture. This is shown also in Table 5-4 by comparison of σ and average values of α for sorption onto Hagerstown silt loam.

The findings presented herein suggest that organic solute sorption onto soil can be affected by organic solvent present in the aqueous phase. Sorption partition coefficients observed in the laboratory isotherm studies are semi-logarithmically inversely related to the volume fraction of solvent for the systems reported in this study. The solvent effect can be quantified, and an estimate of the partition coefficient can be developed from knowledge of solvent volume fraction, the power-term for the semi-logarithmic solubility expression and an average value of the regression-fitted parameter α.

Effect of Organic Carbon Content

The sorption partition coefficients, K_p, for naphthalene sorption onto three soils, Hagerstown silt loam (OC = 1.94%), Berkeley silt loam (OC = 2.81%), and Tifton sand (OC = 0.5%), were determined. The sorption isotherm experiments were performed as described previously with the samples being determined in triplicate and analyzed by HPLC. The liquid phase contained either 0% methanol or 20% by volume methanol. Figures 5-9 and 5-10 show

Table 5-3: Calculated α Values

Solute	Solvent	Solvent [% vol.]	K_p [mole/kg]	α
Hagerstown Silt Loam				
Naphthalene	Methanol	0	443	-
"	"	20	197	0.46
"	"	40	77.6	0.50
"	"	50	28.0	0.63
"	Acetone	10	241	0.52
"	"	30	77.1	0.49
"	"	40	42.6	0.50
"	"	50	17.3	0.55
Naphthol	Methanol	0	410	-
"	"	20	232	0.41
"	"	50	56.1	0.57
Quinoline	Methanol	0	238	-
"	"	20	123	0.50
"	"	50	56.1	0.44
3,5-Dichloroaniline	Methanol	0	138	-
"	"	20	64.1	0.57
"	"	50	20.2	0.57
Berkeley Silt Loam				
Naphthalene	Methanol	0	471	-
"	"	20	217	0.44
Tifton Sand				
Naphthalene	Methanol	0	111	-
"	"	20	49.3	0.46

Average α = 0.51

Standard deviation = 0.060

Table 5-4: Effect of Solvent on Solute Solubility and Sorption Partition Coefficient for Hagerstown Silt Loam

Solute	Solvent	σ*	a	$a\sigma$**
Naphthalene	Methanol	3.79	0.50	1.90
Naphthalene	Acetone	5.14	0.51	2.62
Naphthol	Methanol	3.01	0.49	1.47
Quinoline	Methanol	2.86	0.47	1.34
3,5-Dichloroaniline	Methanol	2.96	0.57	1.69

* Logarithmic increase in mole fraction solute solubility with volume fraction solvent

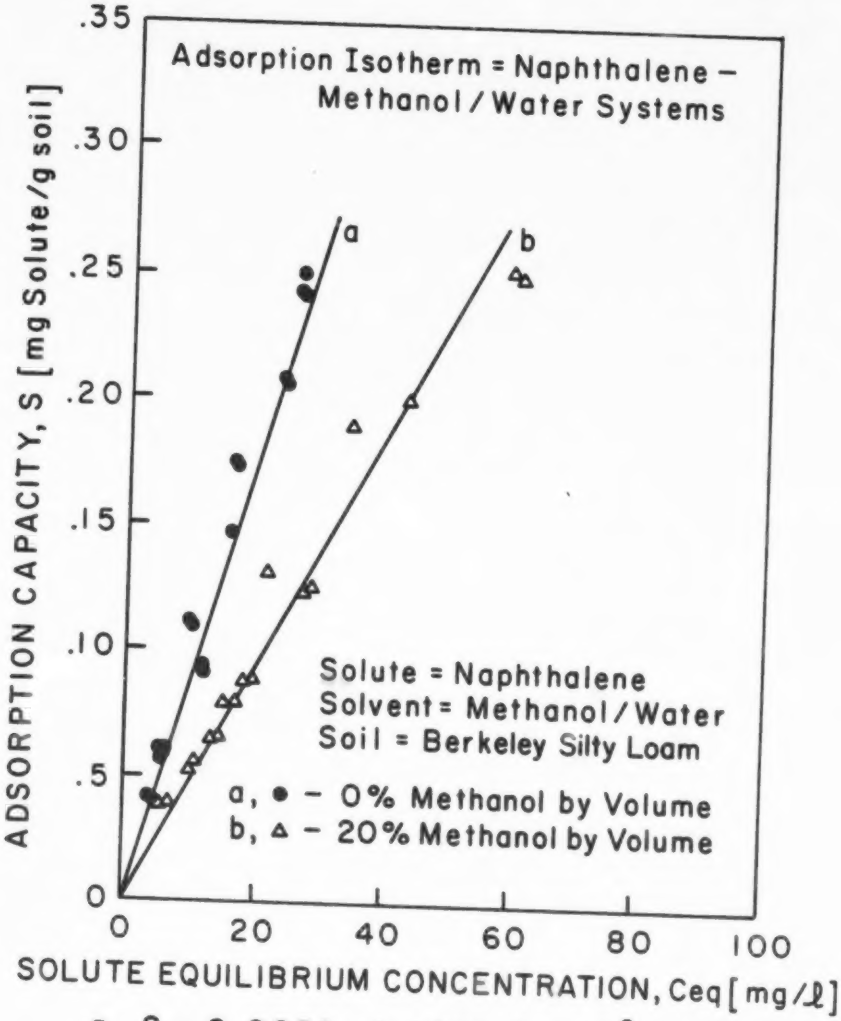
** Logarithmic increase in sorption partition coefficient with volume fraction solvent the results for naphthalene sorption onto Berkeley silt loam and Tifton sand respectively.

Linear least-square regression was performed on the data for these systems, and a trend of increasing sorption partition coefficient with increasing sorbent organic carbon content was observed for the pure water systems: K_p for Tifton sand (OC = 0.5%), Hagerstown silt loam (OC = 1.94%), and Berkeley silt loam (OC = 2.85%) were 2.0 l/kg, 8.0 l/kg and 8.1 l/kg respectively. These data were incorporated in the relationship between K_{oc} and K_{ow} as was shown in Equation 5-23. The trend of increasing values of K_p with increasing OC was also evident in tests with 20% by volume methanol/water mixtures, where K_p values for Tifton sand, Hagerstown silt loam and Berkeley silt loam were 1.0 l/kg, 4.0 l/kg and 4.4 l/kg respectively. These results are plotted in Figure 5-11. Linear least-square regression was performed for the naphthalene sorption partition coefficients for the three soils in two different solvent-water combinations (0% and 20% methanol) versus the organic carbon content of the sorbents. These results are shown in Figure 5-12. The a values for sorption of naphthalene in Berkeley silt loam and Tifton sand may be calculated as 0.44 and 0.46 respectively, as reported in Table 5-3. The limited data suggest that sorption partition coefficient increases in proportion to the sorbent organic carbon content for solvent/water systems.

The Effect of Solvent on Soil Organic Carbon

Results in Chapter 4 explained the effect of solvent/water mixtures on aromatic solute solubility. Results in this chapter have presented a theory for interpreting sorption data in solvent/water systems, and the experimental results have shown how the presence of solvent in the aqueous phase affects partitioning onto soil. An important conclusion from this investigation is that the semi-logarithmic decrease in sorption coefficient with increase solvent volume fraction is about half of that which would be predicted on the basis of semi-logarithmic increase in mole fraction solubility. An explanation for

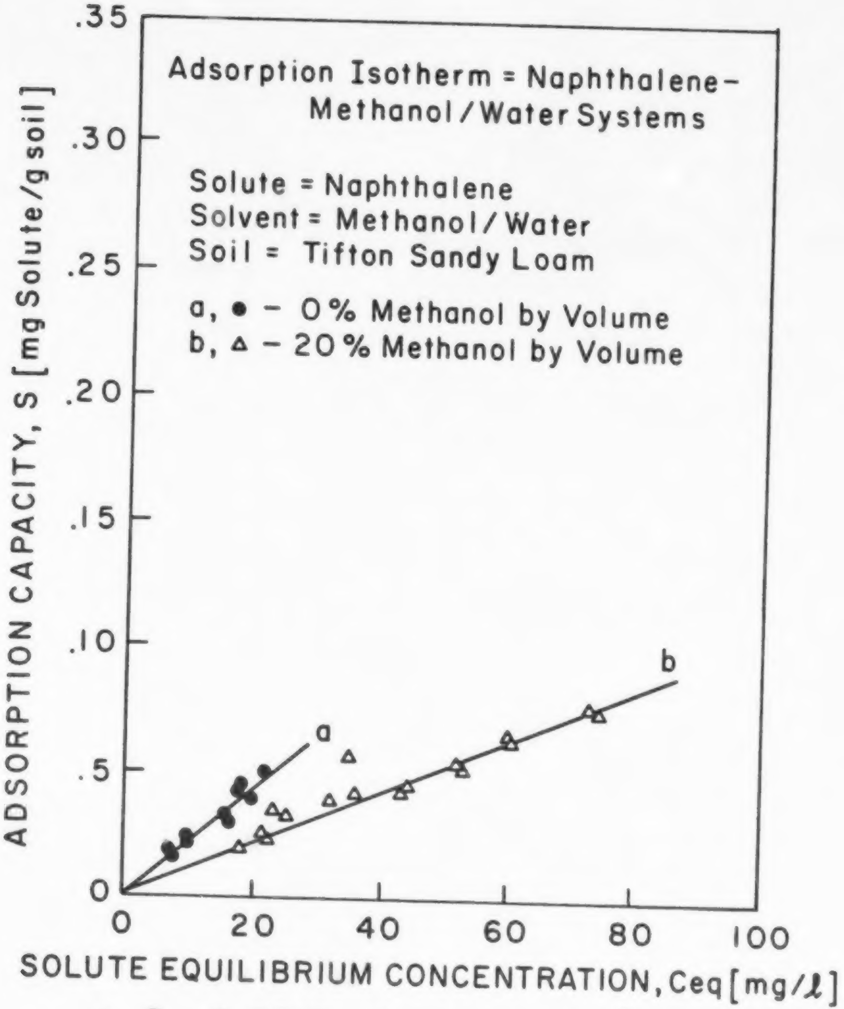
Figure 5-9: Naphthalene Sorption onto Berkeley Silt Loam in Methanol/Water Mixtures



a. $S = 0.0052 + 0.0085\ Ceq$ $R^2 = 95.3\%$

b. $S = 0.0111 + 0.0044\ Ceq$ $R^2 = 94.2\%$

Figure 5-10: Naphthalene Sorption onto Tifton Sand in Methanol/Water Mixtures



a. $S = 0.0013 + 0.0020\ \text{Ceq}$ $R^2 = 87.7\%$

b. $S = 0.0049 + 0.0010\ \text{Ceq}$ $R^2 = 96.0\%$

Figure 5-11: Naphthalene Sorption onto Soils in Methanol/Water Mixtures

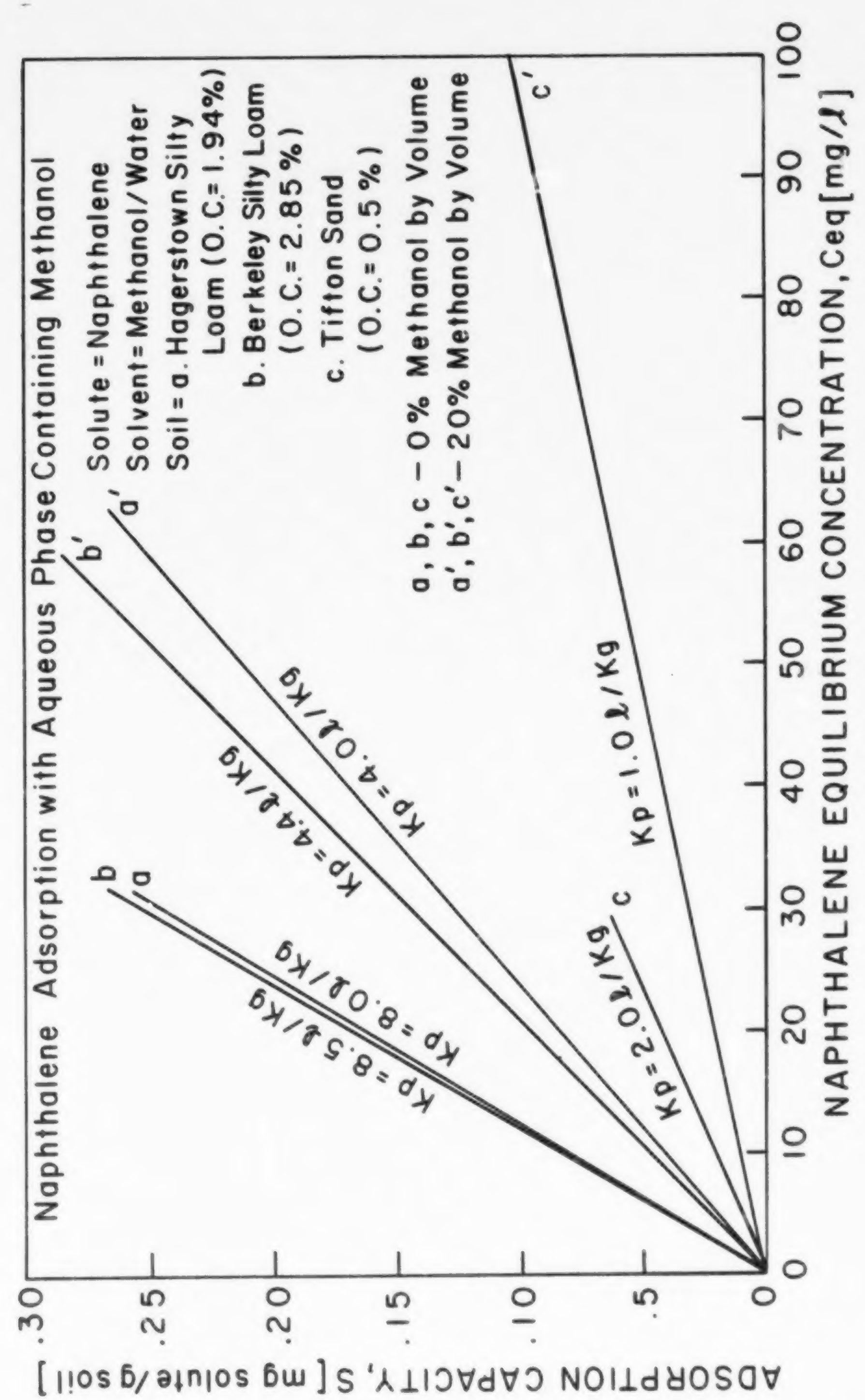
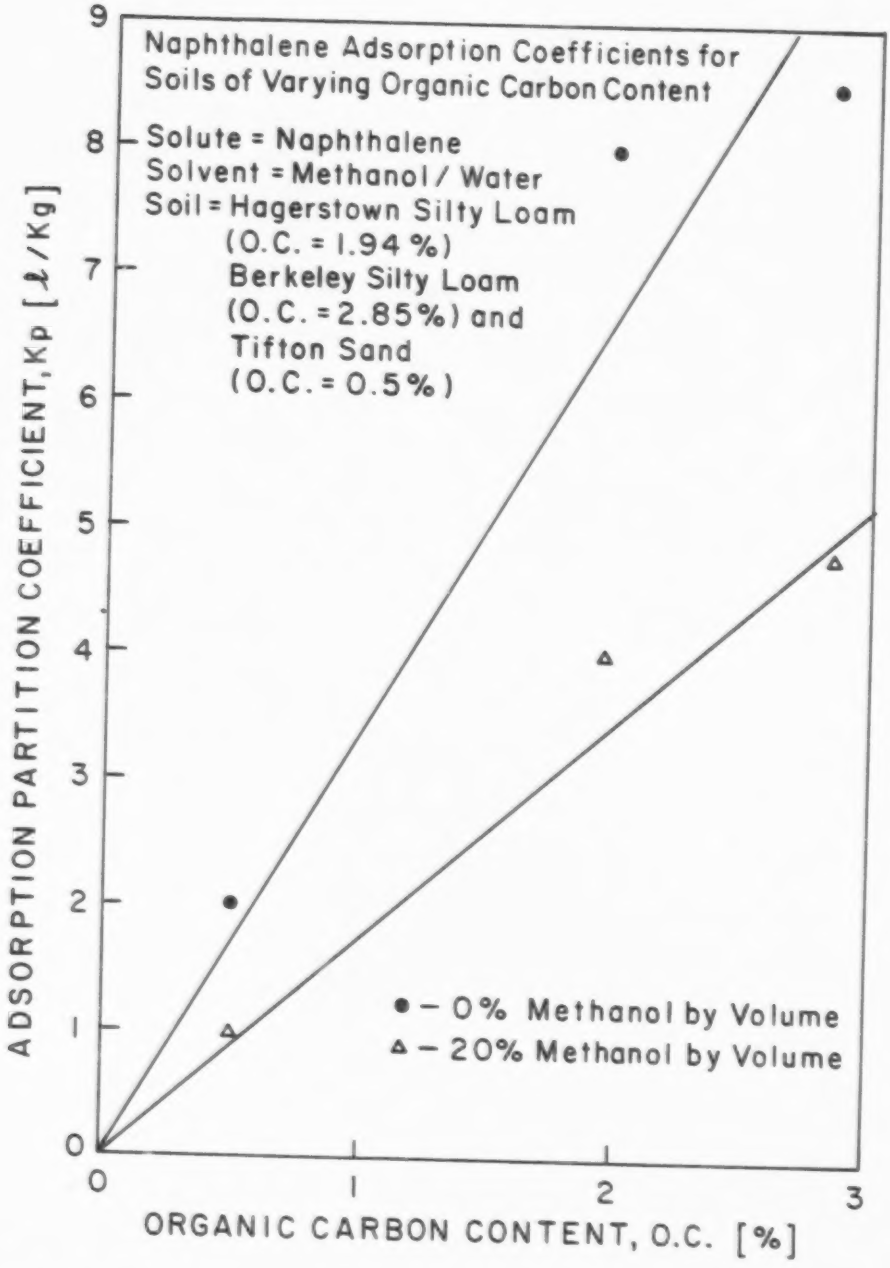


Figure 5-12: Sorbent Organic Carbon Content Effect on Naphthalene Sorption onto Soils in Methanol/Water Mixtures



this phenomena requires understanding of the effect of polar solvent on natural organic carbon of soils.

Freeman and Cheung (1981) explain that the organic carbon in soils/sediments may be envisioned as nonpolar polymeric material, referred to as humin or kerogen, which is chemically bound to the mineral matter. The polymeric material is thought to be highly branched and cross linked to form a three dimensional network. These properties prevent the organic matter from dissolving into water, although liquid may be absorbed, or imbibed. The absorption of liquid would be accompanied by the network swelling to form a gel. The amount of gel swelling depends on the "network compatibility" with the liquid, and the maximum gel swelling is dependent on the extent of cross linkage. Solute preference for either the solution phase or cross linked organic carbon phase depends on competing attractive effects between solute-liquid and solute-gel interactions. Gel swelling is expected to increase as the Hildebrand solubility parameter for the liquid approaches that for the organic carbon gel, which is estimated on the basis of correlations between K_p and K_{ow} to have $\delta \approx 10.3$. These concepts were evaluated by Freeman and Cheung (1981) through liquid chromatographic experiments with columns packed with sediment and soil. This type of phenomenon was also studied by Wending and Yen (1980) who evaluated the swelling of coal with several solvents and solvent/water mixtures. Freeman and Cheung concluded from their work, and the work of Wending and Yen, that soil cross-linked polymer was not readily soluble in solvent, but that solvent causes it to swell. It was suggested that solute diffusion through the swollen gel should be more effective than that through the more densely entangled structure of an incompletely swollen gel.

The sorption experiments described in this chapter were performed with liquid phase having solubility parameters that ranged from 23.50 (100% water) to 19.31 (50% by volume methanol/water) and 16.71 (50% by volume acetone/water). On the basis of the results reported by Freeman and Cheung, it is expected that the organic matter in soil would increase in swelling with decrease in liquid phase solubility parameter. This would result in greater accessibility of the solute to the humin-kerogen polymers in the presence of solvent/water mixtures. This phenomenon would then exert a competing effect that may enhance sorption in contrast to increased solute solubility effects. It is concluded from experimental results reported in this chapter that this phenomenon may account for the observation that the decrease in sorption partition coefficient is less than that predicted from consideration of only solute solubility effects.

Summary

The hydrophobic sorptive behavior of four aromatic solutes onto three different soils with solvent/water mixtures was studied. The sorption isotherm data showed a linear relationship between equilibrium concentration and sorption capacity for systems containing only solute and water, as well as for systems containing solute in solvent/water mixtures.

The effect of polar solvent in the aqueous phase on aromatic solute sorptive behavior was evaluated by theoretical considerations and demonstrated through experimentation. It was observed that the sorption partition coefficients, expressed in units of mole/kg, decreased semi-logarithmically with increase in volume fraction of solvent in the aqueous phase. The results were interpreted by a theory which related the relative magnitude of decrease of the sorption partition coefficient to the increase in solute solubility for miscible solvent/water systems. This entailed estimating or measuring the effect of polar solvent (methanol or acetone) on solute solubility and sorbent sorptive behavior. These results were expressed in terms of the parameter σ which is the logarithmic term with which solute solubility increases with volume fraction solvent in water, and the value of $\alpha\sigma$ which is the logarithmic term with which sorbent sorption coefficient decreases with volume fraction solvent in water. An important conclusion from this evaluation was that the parameter α was typically in the range of

0.45 to 0.55 with an average value of 0.51. This suggests that the semi-logarithmic manner with which sorption partition coefficient decreases with solvent volume fraction is less than the semi-logarithmic manner with which solute solubility increases with solvent volume fraction. The magnitude of the a values show that the logarithmic decrease of sorption partition coefficient is about half of that which could be expected on the basis of the logarithmic increase in solute solubility in the solvent/water mixtures. This may be a result of the solvent/water mixture interacting with natural soil organic carbon and swelling the organic carbon associated with the soil, and thereby increasing solute accessibility to the organic matter. It was shown that the more hydrophobic the solute, the greater the effect of solvent in solvent/water mixtures on solute solubility enhancement, and hence the less the tendency to sorb onto soil. Thus the results of this investigation are particularly significant for those aromatic solutes exhibiting lowest aqueous phase solubility.

Chapter 6

SUMMARY AND CONCLUSION

Summary

This report presented results of an investigation to evaluate the solubility of relatively hydrophobic aromatic solutes in an aqueous phase containing miscible polar organic solvent, and to determine the effect of polar solvent in the aqueous phase on sorption of aromatic solutes onto soils. The investigation was comprised of both theoretical and experimental developments. The results from the solubility experiments were interpreted by means of chemical thermodynamic models to predict solute solubility in solvent/water systems, and the results of the soil sorption studies were evaluated by a model that related reduction in sorption coefficient with increase in solubility.

The subject of aromatic solute solubilization and sorption in miscible solvent/water systems is important for understanding pollutant chemical and physical properties in heavily contaminated industrial wastewaters and in hazardous wastes. These types of wastewaters and wastes may contain appreciable quantities of polar organic solvents which can affect physicochemical properties of aromatic solutes including solubility and phase partitioning.

The phenomenon of aromatic solute solubility in solvent/water systems was evaluated for eighteen systems. This included four types of solvent/water mixtures and seven solutes. The phenomenon of phase partitioning in solvent/water systems was evaluated for aromatic solute sorption onto soil. This entailed batch sorption experiments with methanol/water and acetone/water mixtures with four aromatic solutes and three soils. The soil sorption studies are useful for understanding some aspects of near-source groundwater contamination problems, as in situations for which the release of hydrophobic organic contaminant from spill or other discharge may be accompanied by the release of water-soluble organic solvents. In these instances, the process of solubilization, sorption and transport of hydrophobic organic solutes may be influenced strongly by the presence of comparatively high concentrations of miscible solvent.

The aromatic solutes employed for study of solubility in solvent/water systems were selected to represent different physico-chemical properties with respect to hydrophobicity, polarity, hydrogen bonding and functional group substitution. The solutes ranged in aqueous solubility from about 1 mg/l for phenanthrene to 34,100 mg/l for aniline. The studies showed that the presence of appreciable (i.e. percent by volume) concentration of organic solvent in the aqueous phase can have a very large effect on solubility. In general it was observed that there was a semi-logarithmic increase in solubility with increasing solvent volume fraction. This confirmed a trend predicted from adaptation of regular solution theory wherein logarithmic mole fraction solubility is proportional to solvent volume fraction. The prediction holds for systems for which the solubility parameter of the solute is approximately three units less than that for the solvent. This log-linear approach was the most easily applied of the various techniques which were developed to predict solubility. However, application of the log-linear model requires at least two data points, preferably solubility in pure water and solubility in 50% or 100% pure solvent. While aqueous solubility is commonly available for many aromatic solutes, relatively little information exists on solubility of aromatic compounds in various solvents. If solvent solubility data are lacking, then solubility in solvent may be estimated from prediction of solute infinite dilution activity coefficient as discussed below.

The UNIFAC solution-of-groups model was shown to be useful for predicting solute infinite dilution activity coefficients in solvent/water mixtures. The infinite dilution activity coefficient could then be related to solute solubility through several techniques depending on the value of the activity coefficient and on whether the solute exists as a solid or liquid at the system temperature. This approach was unique among the various predictive techniques in that it did not require specific measurements to obtain correlation coefficients or other parameters. The procedure employs a solution-of-groups concept for which the activity coefficient is estimated from surface area and interaction parameters available in the literature, plus specification of the mole fraction solvent composition and the functional groups comprising the solute, solvent and water. This procedure predicted solute solubility in pure water and in 100% solvent within a factor of two for a range of solute solubilities spanning approximately six orders of magnitude. The accuracy of the prediction of solute solubility in the various eighteen solvent/water systems was 321%, where a value of 100% represents perfect estimation. It was concluded that this approach is a versatile and generally applicable technique for predicting solute solubility in solvent/water systems. However, it needs to be evaluated for systems containing functional groups not considered in this study; also, it is limited in that interaction parameters are available for only certain systems.

If the solute functional group interaction parameters are not available in the UNIFAC data base, then an excess free energy approach is useful for estimating solute solubility. This technique requires knowledge of solvent-water interaction constants, which may be estimated from prediction of solute free-solvent/water activity coefficients. The technique also requires knowledge of a solute interaction constant which may be obtained from correlation of experimental data with solute octanol/water partition coefficient. The excess free energy model accounted for some of the variation in the experimental data from a log-linear relationship. The accuracy for prediction with the eighteen solute-solvent/water systems was

174%. The excess free energy approach was computationally more cumbersome than either the log-linear approach or the approach based on estimation of infinite dilution activity coefficient. Also, it required the use of experimental data and an empirical correlation. For these reasons it is not preferred if either of the other two approaches may be employed.

A molecular surface area technique was shown to predict solute solubility with an accuracy of about 250% for one solute-solvent/water system. This technique is based on consideration of hydrophobic surface area (HSA) and polar surface area (PSA) of the solute, and interfacial free energy terms for water and solvent. At present, this approach is limited because in the absence of experimental data, the proportion of solute total surface area attributable to HSA and PSA is not generally known, and because of the lack of information on the interfacial energy terms for all but a few solvents.

The sorptive behavior of four aromatic solutes onto three different soils with miscible solvent/water mixtures was studied. The sorption isotherm data showed a linear relationship between equilibrium concentration and sorption capacity for systems containing solvent/water mixtures in the liquid phase. It was observed that the sorption partition coefficients, expressed in units of mole/kg, decreased semi-logarithmically with increase of volume fraction of solvent in the aqueous phase. These results were interpreted by a theory which related the relative magnitude of decrease of sorption partition coefficient to the increase in solute solubility. This entailed estimating or measuring the effect of polar solvent (methanol or acetone) on solute solubility and solute sorptive behavior. The results were expressed in terms of the parameter σ which is the logarithmic term with which solute solubility increases with volume fraction solvent in water, and the value of $\alpha\sigma$ which is the logarithmic term with which solute sorption partition coefficient decreases with volume fraction solvent in water. An important observation from this work was that the parameter α was typically in the range of 0.45 to 0.55 with an average value of 0.51. This suggests that the semi-logarithmic manner with which sorption partition coefficient decreases is less of a consequence than the semi-logarithmic manner with which solute solubility increases with solvent volume fraction. The magnitude of the a values shows that the logarithmic change of sorption partition coefficient decrease is about half of that which would be expected on the basis of the logarithmic increase in solute solubility in the solvent/water mixtures. This may be a result of the solvent/water mixture interacting with natural soil organic carbon and swelling the organic carbon associated with the soil, thereby increasing solute accessibility to the organic matter.

It was shown that the more hydrophobic the solute, the greater the effect of the solvent in water on solubility enhancement with concomitant decrease in soil sorption partition coefficient. Hence, the results of this investigation are particularly significant for predicting physico-chemical and soil sorption characteristics for those aromatic pollutants that exhibit lowest aqueous solubility.

Conclusion

Hydrophobic aromatic solutes display a semi-logarithmic increase in solubility with increasing volume fraction of solvent in solvent/water mixtures. This results in a semi-logarithmic decrease in tendency for these solutes to sorb onto soil. The increase in solubility does not result in a directly proportional decrease in sorption coefficient for the solutes studied in this investigation. The increase in solubility in solvent/water mixtures and the decrease in sorption partition coefficients may be predicted by thermodynamic models. This information is useful for assessment of near-source transport of hydrophobic aromatic solutes in soil systems in the event of spill or discharge of hydrophobic solutes with polar solvent. The predictive techniques developed in this investigation may be useful in other applications in environmental engineering, such as for estimation of aromatic solute solubility in heavily contaminated industrial wastewaters, or for evaluation of solute properties for use in analytical procedures.

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Appendix A

EXAMPLE CALCULATION OF ACTIVITY COEFFICIENT USING UNIFAC

The behavior of an organic solute in a multicomponent mixture can be determined by the solute and solvent physical and chemical properties. This Appendix presents the use of the UNIFAC group contribution model for prediction of the solute infinite dilution activity coefficient. Some of the available functional group data are used in the sample calculation. A complete listing of the available functional group interaction data can be found in Gmehling et al. (1982).

The following example shows the steps for calculating the solute infinite dilution activity coefficient. This example considers a three component system: methanol (1, co-solvent), naphthalene (2, solute), and water (3). Using the functional group classification data base (Gmehling et. al, 1982), methanol (CH_3OH) can be considered as one CH_3OH group, and naphthalene ($C_{10}H_8$) may be divided into 8 ACH groups and 2 AC groups, and water can be considered as one H_2O group. The solute activity coefficient can be estimated by Equation 2-19. The functional group parameters shown in Table A-1 are required to perform the calculation for obtaining the combinatorial of solute infinite dilution coefficient From Equation 2-20

$$\ln \gamma_i^c = \ln \frac{\phi_i}{X_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{X_i} (X_1 l_1 + X_2 l_2 + X_3 l_3)$$

where r and q terms cab be calculated by Equation 2-22

$$r_2 = \sum_k \nu_k^2 R_k = \nu_{10}^2 R_{10} + \nu_{11}^2 R_{11} + \nu_{16}^2 R_{16} + \nu_{17}^2 R_{17}$$

$$= 8\ (0.5313) + 2\ (0.3652) + 0\ (0.3682) + 0\ (0.920) = 4.9808$$

$$r_1 = 1\ (1.4311) + 0\ (0.5313) + 0\ (0.3632) + 1\ (0.920) = 1.4311$$

Table A-1: Functional Group Parameters for Methanol, Naphthalene and Water

Group Component		Main group No.	Sub-group No.	ν_k	R_k	Q_k
CH_3OH	1	6	16	1	1.4311	1.432
ACH	2	3	10	8	0.5313	0.400
AC	2	3	11	2	0.3652	0.120
H_2O	3	7	17	1	0.920	1.40

$$r_3 = 0\ (1.4311) + 0\ (0.5313) + 0\ (0.3632) + 1\ (0.920) = 0.920$$

$$q_2 = \sum_k \nu_k^2\ Q_k = \nu_{10}^2\ Q_{10} + \nu_{11}^2\ Q_{11} + \nu_{16}^2\ Q_{16} + \nu_{17}^2\ Q_{17}$$

$$= 8\ (0.400) + 2\ (0.120) + 0\ (4.432) + 0\ (1.40) = 3.44$$

$$q_1 = 1\ (1.432) + 0\ (0.400) + 0\ (0.120) + 0\ (1.40) = 1.432$$

$$q_3 = 0\ (1.432) + 0\ (0.400) + 0\ (0.120) + 1\ (1.40) = 1.40$$

$$l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1) = \frac{10}{2}(4.9808 - 3.44) - (4.9808 - 1) = 3.7232$$

$$l_1 = \frac{10}{2}(1.4311 - 1.432) - (1.4311 - 1) = 0.4356$$

$$l_3 = \frac{10}{2}(0.920 - 1.40) - (0.920 - 1) = 2.32$$

For computation of the infinite dilution activity coefficient of naphthalene in

50% (by volume) methanol and 50% (by volume) water mixture, the mole fraction of methanol is $X_1 = 0.3085$, the mole fraction of naphthalene is $X_2 = 0$, and the mole fraction of water is $X_3 = 0.6915$.

$$\frac{\phi_2}{X_2} = \frac{r_2}{r_1X_1+r_2X_2+r_3X_3} = \frac{4.9808}{1.4311(0.3085)+4.9808(0)+0.920(0.6915)} = 4.6218$$

$$\frac{\theta_2}{\phi_2} = \frac{\dfrac{q_2\ X_2}{q_1X_1+q_2X_2+q_3X_3}}{\dfrac{r_2\ X_2}{r_1X_1+r_2X_2+r_3X_3}} = \frac{q_2}{r_2}\ \frac{r_1X_1+r_2X_2+r_3X_3}{q_1X_1+q_2X_2+q_3X_3}$$

$$= \frac{3.44}{4.9808}\left(\frac{1.4311\ (0.3085) + 4.9808\ (0) + 0.92\ (0.6915)}{1.432\ (0.3085) + 3.44\ (0) + 1.40\ (0.6915)}\right) = 0.5279$$

$$\ln\ \gamma_2^{C} = \ln\ 4.6218 + \frac{10}{2}(3.44)\ \ln\ (1.687) + 3.7232$$

$$- 4.6218\ [0.3085(0.4356) + 0(3.7232) + 0.6915(-2.32)]$$

$$\ln\ \gamma_2^{C} = 2.3016$$

Table A-2 shows the functional group interaction parameters which are used to calculate the residual contribution of the solute infinite dilution activity coefficient. The functional group interaction energy, ψ, is calculated using Equation 2-27 The residual part of the infinite dilution activity coefficient can be calculated using Equation 2-24

$$\ln\ \gamma_2^{R} = \nu_{10}^{2}\ (\ln\Gamma_{10} - \ln\Gamma_{10}^{2}) + \nu_{11}^{2}(\ln\Gamma_{11}^{2} - \ln\Gamma_{11}^{2})$$

$$+ \nu_{16}^{2}\ (\ln\Gamma_{16} - \ln\ \Gamma_{16}^{2}) + \nu_{17}^{2}\ (\ln\Gamma_{17} - \ln\Gamma_{17}^{2})$$

where $\ln\ \Gamma_k$ can be calculated using Equation 2-25. $\ln\ \Gamma_K^2$ can be calculated using Equation 2-25 assuming pure naphthalene for which $X_2 = 1$, thus mole fractions of methanol and water are zero ($X_1 = 0$ and $X_3 = 0$). For naphthalene at infinite dilution in 50% by volume methanol/water mixture, Θ and X can be calculated using Equation 2-26.

Table A-2: Functional Group Interaction Parameters

Main Group No.		6 CH_3OH	3 ACH	3 AC	7 H_2O
6	CH_2OH	0	-50	-50	-181
3	ACH	637.3	0	0	903.8
2	AC	637.3	0	0	903.8
7	H_2O	362.3	362.3	289.6	0

Table A-3: Functional Group Interaction Energy

Subgroup No.		16 CH_3OH	10 ACH	11 AC	17 H_2O
16	CH_3OH	0	1.1827	1.1827	1.8356
10	ACH	0.1178	0	0	0.04817
11	AC	0.1178	0	0	0.04817
17	H_2O	0.2965	0.295	0.3784	0

For naphthalene in infinite dilution ($X_2 = 0$)

$X_{10} = 0$ $\quad X_{11} = 0$ $\quad X_{16} = 0.3085$ $\quad X_{17} = 0.6915$

$\Theta_{10} = 0$ $\quad \Theta_{11} = 0$ $\quad \Theta_{16} = 0.3133$ $\quad \Theta_{17} = 0.6867$

let $A = \Theta_{10}\Psi_{10,10} + \Theta_{11}\Psi_{11,10} + \Theta_{16}\Psi_{16,10} + \Theta_{17}\Psi_{17,10}$

$B = \Theta_{10}\Psi_{10,11} + \Theta_{11}\Psi_{11,11} + \Theta_{16}\Psi_{16,11} + \Theta_{17}\Psi_{17,11}$

$$C = \Theta_{10} \Psi_{10,16} + \Theta_{11} \Psi_{11,16} + \Theta_{16} \Psi_{16,16} + \Theta_{17} \Psi_{17,16}$$

$$D = \Theta_{10} \Psi_{10,17} + \Theta_{11} \Psi_{11,17} + \Theta_{16} \Psi_{16,17} + \Theta_{17} \Psi_{17,17}$$

$$\ln \Gamma_{10} = \Theta_{10} [1 - \ln A - \frac{\Theta_{10} \Psi_{10,10}}{A} - \frac{\Theta_{11} \Psi_{10,11}}{B} - \frac{\Theta_{16} \Psi_{10,16}}{C} - \frac{\Theta_{13} \Psi_{10,17}}{D}]$$

$$= 0.4 (1+0.5549 -0 -0 - 0.06439 - 0.0262) = 0.585)$$

$$\ln \Gamma_{11} = 0.1757$$

For pure naphthalene ($X_2 = 1$)

$$X_{10} = 0.8 \qquad X_{11} = 0.2 \qquad X_{16} = 0 \qquad X_{17} = 0$$

$$\Theta_{10} = 0.5714 \qquad \Theta_{11} = 0.4286 \qquad \Theta_{16} = 0 \qquad \Theta_{17} = 0.$$

using Equation 2-25, and

$$\ln\Gamma_{10}^{2} = 0$$

$$\ln\Gamma_{11}^{2} = 0$$

$$\ln \gamma_2^R = \nu_{10}^{2} [\ln\Gamma_{10} - \ln\Gamma_{10}^{2}] + \nu_{11}^{2} [\ln\Gamma_{11} - \ln\Gamma_{11}^{2}]$$

$$= 8 (0.5857-0) + 2 (0.1757-0) = 5.037$$

The combinatorial and residual contributions to the infinite dilution activity coefficient are added as in Equation 2-19

$$\ln \gamma_2^{\infty} = \ln \gamma_2^{C} + \ln\gamma_2^{R}$$

$$\ln \gamma_2^{\infty} = 2.3061 + 5.037 = 7.3386$$

$$\gamma_2^{\infty} = 1538.56$$

This value of γ_2^{∞} was obtained by hand calculation, and it agrees with a computer calculation as shown in Table 4-2 to three significant figures.

Appendix B

PREDICTION OF SOLUTE SOLUBILITY BY THE UNIFAC APPROACH, THE LOG-LINEAR APPROACH, AND THE EXCESS FREE ENERGY APPROACH

Table B-1: Naphthalene Solubility in Methanol/Water Mixtures

Solvent Mole Frac.	Solvent Volume Frac.	UNIFAC Mole Frac. Sol.	Excess Free Energy Mole Frac. Sol.	Log-linear Mole Frac. Sol.	UNIFAC Sol.	Excess Free Energy Sol.	Log-linear Sol.
[-]	[-]	[-]	[-]	[-]	[mg/l]	[mg/l]	[mg/l]
.0000	.0000	.0000020	.0000043	.0000043	14.40	30.57	30.57
.0500	.1764	.0000114	.0000223	.0000293	69.80	136.88	180.35
.1000	.3114	.0000251	.0001307	.0001272	136.18	708.98	690.14
.1500	.4180	.0000674	.0006167	.0004054	327.37	2988.46	1966.01
.2000	.5043	.0001453	.0022046	.0010362	638.56	9615.35	4538.40
.2500	.5756	.0002934	.0061122	.0022505	1176.86	24068.98	8969.85
.3000	.6356	.0005452	.0137140	.0043179	2010.66	48754.86	15755.06
.3500	.6866	.0009486	.0259555	.0075232	3236.38	83255.09	25245.70
.4000	.7307	.0015658	.0429204	.0121424	4968.46	124361.30	37614.05
.4500	.7690	.0024780	.0637905	.0184251	7344.59	167646.00	52854.18
.5000	.8027	.0039205	.0871343	.0265819	10891.85	209120.30	70810.34
.5500	.8326	.0059080	.1113104	.0367779	15433.40	246058.40	91219.27
.6000	.8592	.0087350	.1348067	.0491313	21508.72	277039.60	113755.40
.6500	.8831	.0127350	.1564404	.0637149	29614.64	301627.00	138070.70
.7000	.9047	.0183800	.1754247	.0805601	40418.78	320001.10	163825.20
.7500	.9243	.0263500	.1913442	.0996619	54833.75	332676.00	190708.50
.8000	.9421	.0453100	.2040838	.1209846	88484.31	340315.70	218450.70
.8500	.9584	.0670200	.2137450	.1444674	123146.30	343625.50	246828.00
.9000	.9734	.0975800	.2205686	.1700299	168254.40	343293.50	275663.10
.9500	.9872	.1403650	.2248713	.1975763	226281.80	339960.80	304821.40
1.0000	1.0000	.1781000	.2270000	.2270000	271301.50	334206.80	334206.80
.0266	.1001	.0000044	.0000097	.0000128	28.86	63.78	83.90
.0578	.1998	.0000098	.0000295	.0000378	59.04	177.85	227.79
.0952	.2998	.0000227	.0001111	.0001122	124.67	609.42	615.57
.1406	.3997	.0000548	.0004706	.0003323	271.46	2327.34	1644.28
.1971	.4997	.0001391	.0020626	.0009862	614.63	9050.11	4343.69
.2691	.5997	.0003751	.0085131	.0029241	1455.63	32242.37	11261.12
.3642	.6998	.0010990	.0303136	.0086798	3671.29	94443.91	28462.80
.4953	.7997	.0037680	.0848791	.0257305	10530.48	205382.90	69013.32
.6884	.8999	.0168940	.1712837	.0764503	37632.45	316268.30	157738.90
.2320	.5514	.0002303	.0043486	.0017297	953.56	17763.95	7126.74
.2874	.6214	.0004650	.0113856	.0037009	1750.25	41536.84	13801.08
.3470	.6838	.0009190	.0250840	.0072936	3149.76	80957.10	24595.94
.3749	.7093	.0012246	.0338458	.0096304	4027.69	103170.50	31041.85
.4457	.7659	.0023855	.0618755	.0178138	7110.94	163945.50	51433.72
.4974	.8011	.0038355	.0858858	.0261087	10690.71	207057.70	69813.55
.5541	.8349	.0061040	.1132812	.0377084	15866.97	248834.30	92991.85
.6157	.8670	.0098450	.1418453	.0534681	23806.16	285449.30	121215.20

Table B-1: continued

Solvent Mole Fraction	Solvent Volume Fraction	Molecular Surface Area Solubility	Molecular Surface Area Solubility
[-]	[-]	[-]	[mg/l]
.0000	.0000	.0000043700	31.00
.0472	.0999	.0000107442	72.00
.1003	.1999	.0000263150	166.00
.1604	.2999	.0000697873	406.00
.2292	.3999	.0001581667	873.00
.3084	.4999	.0003880909	1988.00
1.0000	1.0000	.0373488100	108943.00

Table B-2: Naphthalene Solubility in Acetone/Water Mixtures

Solvent Mole Frac.	Solvent Volume Frac.	UNIFAC Mole Frac. Sol.	Excess Free Energy Mole Frac. Sol.	Log-linear Mole Frac. Sol.	UNIFAC Sol.	Excess Free Energy Sol.	Log-linear Sol.
[-]	[-]	[-]	[-]	[-]	[mg/l]	[mg/l]	[mg/l]
.0000	.0000	.0000020	.0000043	.0000043	14.40	30.57	30.57
.0500	.1764	.0000114	.0000213	.0000281	69.80	131.14	172.80
.1000	.3114	.0000251	.0001212	.0001180	136.18	657.42	639.95
.1500	.4180	.0000674	.0005573	.0003663	327.37	2700.94	1776.71
.2000	.5043	.0001453	.0019507	.0009169	638.56	8515.76	4017.49
.2500	.5756	.0002934	.0053156	.0019572	1176.86	20983.94	7807.97
.3000	.6356	.0005452	.0117544	.0037010	2010.66	42013.13	13527.22
.3500	.6866	.0009486	.0219728	.0063688	3236.38	71158.82	21433.90
.4000	.7307	.0015658	.0359485	.0101700	4968.46	105708.20	31644.23
.4500	.7690	.0024780	.0529336	.0152892	7344.59	141961.90	44137.81
.5000	.8027	.0039205	.0717154	.0218780	10891.85	176569.20	58782.13
.5500	.8326	.0059080	.0909520	.0300513	15433.40	207209.80	75365.42
.6000	.8592	.0087350	.1094414	.0398867	21508.72	232653.90	93630.52
.6500	.8831	.0127350	.1262700	.0514271	29614.64	252516.10	113303.70
.7000	.9047	.0183800	.1408538	.0646841	40418.78	266957.40	134117.10
.7500	.9243	.0263500	.1529083	.0796425	54833.75	276444.80	155823.60
.8000	.9421	.0453100	.1623847	.0962646	88484.31	281586.80	178205.70
.8500	.9584	.0670200	.1694001	.1144952	123146.30	283033.50	201079.30
.9000	.9734	.0975800	.1741736	.1342653	168254.40	281419.60	224293.90
.9500	.9872	.1403650	.1769773	.1554957	226281.80	277333.20	247731.30
1.0000	1.0000	.1781000	.1781000	.1781000	271301.50	271301.50	271301.50
.0266	.1001	.0000044	.0000095	.0000125	28.86	62.25	81.88
.0578	.1998	.0000098	.0000281	.0000360	59.04	169.44	217.01
.0952	.2998	.0000227	.0001033	.0001043	124.67	566.70	572.41
.1406	.3997	.0000548	.0004271	.0003016	271.46	2112.66	1492.53
.1971	.4997	.0001391	.0018271	.0008736	614.63	8023.55	3849.30
.2691	.5997	.0003751	.0073604	.0025282	1455.63	27972.13	9747.96
.3642	.6998	.0010990	.0255804	.0073245	3671.29	80577.16	24097.90
.4953	.7997	.0037680	.0699101	.0211927	10530.48	173457.50	57319.27
.6884	.8999	.0168940	.1376896	.0614560	37632.45	264068.80	129200.30
.2320	.5514	.0002303	.0038041	.0015132	953.56	15567.29	6238.82
.2874	.6214	.0004650	.0097923	.0031830	1750.25	35885.73	11887.59
.3470	.6838	.0009190	.0212497	.0061787	3149.76	69222.79	20895.00
.3749	.7093	.0012246	.0284949	.0081079	4027.69	87914.76	26228.99
.4457	.7659	.0023855	.0513832	.0147931	7110.94	138867.30	42976.34
.4974	.8011	.0038355	.0707161	.0214972	10690.71	174852.10	57970.76
.5541	.8349	.0061040	.0925108	.0307944	15866.97	209501.70	76803.55
.6157	.8670	.0098450	.1149385	.0433257	23806.16	239492.50	99669.19

Table B-3: Naphthalene Solubility in Ethanol/Water Mixtures

Solvent Mole Frac.	Solvent Volume Frac.	UNIFAC Mole Frac. Sol.	Excess Free Energy Mole Frac. Sol.	Log-linear Mole Frac. Sol.	UNIFAC Sol.	Excess Free Energy Sol.	Log-linear Sol.
[-]	[-]	[-]	[-]	[-]	[mg/l]	[mg/l]	[mg/l]
.0000	.0000	.0000020	.0000043	.0000043	14.40	30.57	30.57
.0500	.1453	.0000084	.0000123	.0000166	53.48	78.27	105.82
.1000	.2641	.0000259	.0000339	.0000499	150.21	196.45	289.37
.1500	.3631	.0000652	.0000857	.0001249	346.28	455.30	663.62
.2000	.4468	.0001406	.0001957	.0002714	689.23	959.45	1330.08
.2500	.5185	.0002695	.0004051	.0005277	1226.39	1842.22	2398.99
.3000	.5806	.0004712	.0007668	.0009389	1999.74	3250.69	3977.98
.3500	.6349	.0007655	.0013423	.0015541	3042.61	5325.61	6161.88
.4000	.6829	.0011717	.0021961	.0024241	4378.31	8181.97	9025.55
.4500	.7255	.0017081	.0033899	.0035985	6020.34	11894.93	12619.76
.5000	.7636	.0023915	.0049782	.0051240	7973.77	16493.17	16970.13
.5500	.7979	.0033350	.0070038	.0070423	10544.44	21959.53	22078.46
.6000	.8289	.0044190	.0094967	.0093897	13281.63	28237.23	27925.65
.6500	.8571	.0057200	.0124729	.0121960	16377.20	35239.17	34475.51
.7000	.8829	.0072590	.0159356	.0154843	19836.71	42858.45	41678.93
.7500	.9065	.0090550	.0198762	.0192715	23658.91	50978.23	49477.92
.8000	.9282	.0111300	.0242765	.0235682	27849.49	59479.75	57809.23
.8500	.9482	.0135080	.0291104	.0283796	32417.27	68248.88	66607.52
.9000	.9667	.0162080	.0343463	.0337056	37357.86	77180.29	75807.80
.9500	.9840	.0192480	.0399487	.0395419	42664.95	86180.03	85347.24
1.0000	1.0000	.0226350	.0458800	.0458800	48310.11	95166.72	95166.72
.0419	.1238	.0000068	.0000103	.0000136	44.18	67.12	88.11
.0716	.1994	.0000140	.0000192	.0000274	85.94	117.35	167.54
.1167	.3115	.0000360	.0000524	.0000774	210.75	307.08	453.58
.1705	.3990	.0000908	.0001217	.0001743	466.35	625.28	895.33
.2357	.4990	.0002261	.0003322	.0004407	1050.34	1542.57	2045.75
.3163	.5991	.0005560	.0009278	.0011146	2308.76	3847.62	4619.38
.4185	.6992	.0013541	.0025951	.0028206	4949.71	9453.38	10268.36
.5523	.7994	.0033800	.0071080	.0071406	10661.33	22231.07	22331.43
.7351	.8996	.0084920	.0186529	.0180900	22482.62	48513.26	47095.23
.1419	.3482	.0000568	.0000742	.0001088	305.84	399.87	586.00
.1686	.3929	.0000881	.0001146	.0001648	450.86	586.51	842.72
.2012	.4486	.0001430	.0001994	.0002761	699.65	975.62	1350.57
.2172	.4428	.0001779	.0001881	.0002617	796.21	841.76	1170.48
.2646	.5375	.0003200	.0004923	.0006297	1426.09	2192.58	2802.79
.3589	.6439	.0008291	.0014721	.0016889	3258.43	5774.13	6620.10
.4192	.6998	.0013613	.0026111	.0028364	4972.19	9503.83	10317.38
.5402	.7914	.0031460	.0065707	.0066336	10048.80	20821.92	21018.14
.6591	.8620	.0059820	.0130670	.0127580	16980.26	36583.27	35739.49
.9480	.9833	.0191200	.0397181	.0392987	42446.46	85819.80	84959.86
1.0000	1.0000	.0226350	.0458800	.0458800	48310.11	95166.72	95166.72

Table B-4: Naphthalene Solubility in Propanol/Water Mixtures

Solvent Mole Frac.	Solvent Volume Frac.	UNIFAC Mole Frac. Sol.	Excess Free Energy Mole Frac. Sol.	Log-linear Mole Frac. Sol.	UNIFAC Sol.	Excess Free Energy Sol.	Log-linear Sol.
[-]	[-]	[-]	[-]	[-]	[mg/l]	[mg/l]	[mg/l]
.0000	.0000	.0000020	.0000043	.0000043	14.40	30.57	30.57
.0500	.1735	.0000121	.0000189	.0000224	74.98	116.82	138.30
.1000	.3071	.0000459	.0000709	.0000797	250.58	386.99	435.37
.1500	.4131	.0001282	.0002153	.0002184	627.56	1053.46	1068.61
.2000	.4993	.0002907	.0005396	.0004952	1289.18	2391.33	2194.96
.2500	.5707	.0005671	.0011525	.0009764	2298.34	4662.21	3951.99
.3000	.6309	.0009894	.0021619	.0017297	3690.13	8036.18	6437.60
.3500	.6823	.0015851	.0036543	.0028187	5473.16	12550.54	9701.69
.4000	.7267	.0023763	.0056811	.0042978	7635.36	18113.94	13747.76
.4500	.7655	.0034850	.0082556	.0062101	10464.85	24541.08	18540.52
.5000	.7996	.0047922	.0113568	.0085862	13502.58	31597.53	24016.14
.5500	.8298	.0063710	.0149378	.0114444	16902.51	39039.40	30092.64
.6000	.8568	.0082380	.0189346	.0147923	20643.40	46641.13	36678.88
.6500	.8811	.0104110	.0232749	.0186276	24711.01	54210.95	43681.74
.7000	.9030	.0129050	.0278844	.0229404	29087.58	61596.63	51011.22
.7500	.9229	.0157380	.0326918	.0277144	33765.11	68684.72	58583.85
.8000	.9410	.0189250	.0376315	.0329287	38731.21	75396.25	66324.44
.8500	.9576	.0224870	.0426454	.0385587	43987.48	81681.11	74167.07
.9000	.9729	.0264350	.0476833	.0445778	49517.34	87511.99	82055.27
.9500	.9870	.0307750	.0527030	.0509578	55298.79	92879.18	89941.30
1.0000	1.0000	.0360000	.0576700	.0576700	62130.05	97785.74	97785.74
.0270	.0997	.0000057	.0000097	.0000111	37.61	63.61	72.92
.0588	.1995	.0000158	.0000242	.0000287	95.26	146.19	173.04
.0967	.2992	.0000425	.0000654	.0000740	233.74	359.73	407.14
.1427	.3990	.0001120	.0001854	.0001910	556.57	921.12	949.06
.1998	.4990	.0002898	.0005378	.0004938	1285.90	2384.28	2189.28
.2725	.5991	.0007373	.0015518	.0012777	2876.19	6038.52	4976.24
.3682	.6992	.0018496	.0043286	.0033094	6217.94	14462.37	11085.07
.4997	.7994	.0047840	.0113368	.0085705	13484.46	31553.80	23981.41
.6921	.8997	.0124900	.0271411	.0222278	28378.42	60447.00	49834.95
.0880	.2779	.0000345	.0000526	.0000604	193.47	295.49	339.36
.1051	.3190	.0000516	.0000801	.0000893	278.33	432.49	481.90
.1407	.3951	.0001078	.0001778	.0001840	538.16	887.24	918.09
.2064	.5092	.0003190	.0005996	.0005440	1397.98	2625.20	2382.16
.3191	.6515	.0011951	.0026713	.0021029	4325.33	9628.46	7591.44
.4476	.7637	.0034290	.0081197	.0061080	10329.17	24216.22	18294.27
.6440	.8783	.0101340	.0227384	.0181418	24207.25	53309.67	42822.42
.7993	.9408	.0188880	.0375617	.0328527	38680.04	75305.15	66215.20

Table B-5: Naphthol Solubility in Methanol/Water Mixtures

Solvent Mole Frac.	Solvent Volume Frac.	UNIFAC Mole Frac. Sol.	Excess Free Energy Mole Frac. Sol.	Log-linear Mole Frac. Sol.	UNIFAC Sol.	Excess Free Energy Sol.	Log-linear Sol.
[-]	[-]	[-]	[-]	[-]	[mg/l]	[mg/l]	[mg/l]
.0000	.0000	.0001716	.0001060	.0001060	1367.50	845.27	845.27
.0500	.1055	.0003621	.0001638	.0002238	2715.20	1229.58	1679.28
.1000	.1993	.0006911	.0002631	.0004351	4887.63	1864.92	3081.32
.1500	.2833	.0012307	.0004279	.0007891	8227.92	2872.47	5287.13
.2000	.3590	.0020435	.0006938	.0013488	12937.49	4420.96	8567.55
.2500	.4275	.0032200	.0011110	.0021914	19329.33	6732.54	13215.83
.3000	.4898	.0048560	.0017474	.0034077	27662.99	10086.03	19531.48
.3500	.5468	.0070500	.0026919	.0051005	38133.13	14815.65	27802.37
.4000	.5990	.0124550	.0040570	.0073831	63383.70	21303.94	38286.74
.4500	.6470	.0179350	.0059801	.0103772	86186.95	29967.89	51196.74
.5000	.6914	.0251600	.0086249	.0142103	113931.10	41238.74	66685.25
.5500	.7325	.0342300	.0121812	.0190133	145812.40	55536.01	84837.20
.6000	.7707	.0449260	.0168634	.0249183	179951.90	73238.26	105665.60
.6500	.8062	.0566300	.0229088	.0320564	213633.50	94653.50	129113.00
.7000	.8394	.0686000	.0305745	.0405552	244561.00	119992.40	155057.80
.7500	.8705	.0802100	.0401337	.0505377	271439.70	149348.80	183323.20
.8000	.8996	.0911200	.0518718	.0621204	294076.30	182688.30	213690.00
.8500	.9270	.1012000	.0660819	.0754122	312834.70	219849.30	245909.50
.9000	.9528	.1104200	.0830605	.0905136	328216.50	260553.90	279717.10
.9500	.9770	.1188400	.1031031	.1075156	340806.60	304427.90	314843.80
1.0000	1.0000	.1265300	.1265000	.1265000	351092.10	351027.20	351027.20
.0472	.0999	.0003483	.0001596	.0002151	2620.27	1202.34	1619.56
.1003	.1999	.0006936	.0002638	.0004367	4903.62	1869.71	3091.91
.1604	.2997	.0012205	.0004735	.0008862	8072.99	3143.46	5871.45
.2292	.3998	.0026804	.0009151	.0018010	16448.31	5661.64	11096.72
.3084	.4998	.0051830	.0018818	.0036558	29268.96	10774.56	20776.85
.4008	.5998	.0125300	.0040830	.0074251	63708.00	21424.29	38473.71
.5099	.6998	.0268100	.0092502	.0150800	119955.60	43816.53	70066.41
.6408	.7999	.0544400	.0216826	.0306445	207603.50	90423.29	124606.80
.8005	.8999	.0912400	.0520012	.0622447	294321.20	183041.30	214003.40

Table B-6: Naphthol Solubility in Acetone/Water Mixtures

Solvent Mole Frac.	Solvent Volume Frac.	UNIFAC Mole Frac. Sol.	Excess Free Energy Mole Frac. Sol.	Log-linear Mole Frac. Sol.	UNIFAC Sol.	Excess Free Energy Sol.	Log-linear Sol.
[-]	[-]	[-]	[-]	[-]	[mg/l]	[mg/l]	[mg/l]
.0000	.0000	.0001716	.0001060	.0001060	1367.50	845.27	845.27
.0500	.1764	.0007386	.0003423	.0004071	5089.96	2363.41	2810.24
.1000	.3114	.0024665	.0013533	.0011399	14892.24	8212.15	6923.79
.1500	.4180	.0067370	.0045821	.0025707	35852.03	24589.42	13904.33
.2000	.5043	.0217000	.0123746	.0049667	99723.11	58646.53	24138.11
.2500	.5756	.0480000	.0270204	.0085588	188587.40	112547.90	37642.70
.3000	.6356	.0795000	.0493761	.0135205	270487.40	180367.40	54134.93
.3500	.6866	.1060000	.0782150	.0199614	322343.20	251672.60	73141.91
.4000	.7307	.1279000	.1107015	.0279305	355426.50	317196.10	94109.36
.4500	.7690	.1453000	.1434581	.0374250	375198.00	371522.60	116484.30
.5000	.8027	.1595000	.1735263	.0484013	387032.30	412746.40	139766.50
.5500	.8326	.1715000	.1988796	.0607853	394115.80	441128.10	163533.80
.6000	.8592	.1814000	.2185065	.0744824	397312.40	457969.10	187449.10
.6500	.8831	.1898700	.2322353	.0893850	398185.00	464945.30	211255.20
.7000	.9047	.1970600	.2404677	.1053789	397198.90	463777.80	234765.20
.7500	.9243	.2030500	.2439258	.1223483	394626.10	456089.40	257850.00
.8000	.9421	.2080300	.2434589	.1401789	390858.20	443347.90	280426.90
.8500	.9584	.2120000	.2399151	.1587604	385955.10	426846.30	302448.40
.9000	.9734	.2149500	.2340675	.1779884	379948.70	407699.70	323894.00
.9500	.9872	.2169000	.2265802	.1977651	372905.30	386848.50	344762.90
1.0000	1.0000	.2177000	.2180000	.2180000	364638.90	365068.00	365068.00
.0266	.1001	.0003880	.0001845	.0002274	2855.90	1359.75	1675.63
.0578	.1998	.0009106	.0004248	.0004866	6142.49	2872.76	3289.25
.0952	.2998	.0022190	.0011910	.0010436	13563.86	7314.78	6413.70
.1406	.3997	.0056470	.0037053	.0022358	30769.84	20347.10	12350.15
.1971	.4997	.0204900	.0117531	.0047970	95013.48	56111.40	23453.76
.2691	.5997	.0393953	.0346715	.0102851	154094.80	137346.30	43612.83
.3642	.6998	.1138248	.0872167	.0220685	335995.80	271181.60	78921.97
.4953	.7997	.3430000	.1708770	.0473082	660099.40	409432.70	137551.40

Table B-7: Quinoline Solubility in Methanol/Water Mixtures

Solvent Mole Frac. [-]	Solvent Volume Frac. [-]	UNIFAC Mole Frac. Sol. [-]	Excess Free Energy Mole Frac. Sol. [-]	Log-linear Mole Frac. Sol. [-]	UNIFAC Sol. [mg/l]	Excess Free Energy Sol. [mg/l]	Log-linear Sol. [mg/l]
.0000	.0000	.0005437	.0009610	.0009610	3874.71	6832.62	6832.62
.0500	.1055	.0013743	.0015410	.0019998	9184.38	10289.57	13321.95
.1000	.1993	.0030470	.0025266	.0038382	19095.38	15873.44	23963.94
.1500	.2833	.0062050	.0041480	.0068811	36375.09	24538.22	40219.40
.2000	.3590	.0119330	.0067350	.0116411	65048.37	37500.12	63531.81
.2500	.4275	.0223150	.0107395	.0187372	91788.30	56184.30	95112.49
.3000	.4898	.0259952	.0167562	.0288888	123338.60	82105.11	135720.60
.3500	.5468	.0388383	.0255386	.0429034	170053.30	116674.30	185493.70
.4000	.5990	.0555880	.0380094	.0616613	223650.10	160958.40	243879.90
.4500	.6470	.0766466	.0552633	.0860982	282389.50	215436.60	309695.50
.5000	.6914	.1022798	.0785618	.1171859	344286.70	279826.20	381293.90
.0472	.0999	.0013103	.0014995	.0019238	8788.05	10047.33	12861.90
.1003	.1999	.0030610	.0025342	.0038524	19175.61	15915.14	24043.24
.1604	.2997	.0063030	.0045935	.0077108	36549.58	26835.63	44442.00
.2292	.3998	.0172150	.0088668	.0154574	89503.40	47619.57	80909.25
.3084	.4998	.0261200	.0180154	.0309501	123049.20	87273.59	143448.40

Table B-8: Quinoline Solubility in Acetone/Water Mixtures

Solvent Mole Frac. [-]	Solvent Volume Frac. [-]	UNIFAC Mole Frac. Sol. [-]	Excess Free Energy Mole Frac. Sol. [-]	Log-linear Mole Frac. Sol. [-]	UNIFAC Sol. [mg/l]	Excess Free Energy Sol. [mg/l]	Log-linear Sol. [mg/l]
.0000	.0000	.0005437	.0009610	.0009610	3874.71	6832.62	6832.62
.0266	.1001	.0011842	.0016284	.0019260	7779.03	10673.41	12605.04
.0500	.1764	.0021775	.0028937	.0032729	13357.76	17692.49	19976.21
.0578	.1998	.0026388	.0035334	.0038499	15829.47	21111.05	22969.19
.0952	.2998	.0062430	.0091146	.0077137	33679.62	48618.28	41372.56
.1000	.3114	.0069320	.0102453	.0083591	36888.65	53825.43	44236.82
.1406	.3997	.0162550	.0257021	.0154382	76713.59	117552.30	73060.05
.1500	.4180	.0197200	.0311879	.0175308	90324.02	137710.00	80873.15
.1971	.4997	.0552200	.0734219	.0309407	210232.90	266766.90	125827.90
.2000	.5043	.0595300	.0769360	.0319358	223119.30	275949.80	128882.60
.2500	.5756	.1545000	.1561027	.0524226	440906.80	444124.20	185729.10
.2691	.5997	.1810000	.1955771	.0619712	482890.80	508732.30	209135.00
.3000	.6356	.5105000	.2691330	.0794998	852767.80	608003.90	248362.90
.0266	.1001	.0011842	.0016284	.0019260	7779.03	10673.41	12605.04
.0578	.1998	.0026388	.0035334	.0038499	15829.47	21111.05	22969.19
.0952	.2998	.0062430	.0091146	.0077137	33679.62	48618.28	41372.56
.1406	.3997	.0162550	.0257021	.0154382	76713.59	117552.30	73060.05
.1971	.4997	.0552200	.0734219	.0309407	210232.90	266766.90	125827.90

Table B-9: 3,5-Dichloroaniline Solubility in Methanol/Water Mixtures

Solvent Mole Frac. [-]	Solvent Volume Frac. [-]	UNIFAC Mole Frac. Sol. [-]	Excess Free Energy Mole Frac. Sol. [-]	Log-linear Mole Frac. Sol. [-]	UNIFAC Sol. [mg/l]	Excess Free Energy Sol. [mg/l]	Log-linear Sol. [mg/l]
.0000	.0000	.0000817	.0000872	.0000872	732.27	781.19	781.19
.0500	.1055	.0002266	.0001508	.0002091	1910.52	1271.93	1762.88
.1000	.1993	.0005101	.0002684	.0004552	4057.93	2137.62	3622.48
.1500	.2833	.0010035	.0004795	.0009137	7549.20	3616.36	6876.79
.2000	.3590	.0017922	.0008477	.0017114	12769.82	6065.94	12198.88
.2500	.4275	.0029719	.0014700	.0030205	20081.42	9997.20	20405.61
.3000	.4898	.0046448	.0024894	.0050642	29786.96	16103.65	32421.55
.3500	.5468	.0073730	.0041076	.0081193	44819.07	25279.36	49217.93
.4000	.5990	.0107650	.0065992	.0125180	62066.08	38614.60	71730.45
.4500	.6470	.0152320	.0103258	.0186460	83241.91	57358.85	100763.70
.5000	.6914	.0209870	.0157487	.0269392	108610.20	82842.23	136896.00
.5500	.7325	.0282500	.0234396	.0378792	138283.60	116353.50	180401.20
.6000	.7707	.0372700	.0340888	.0519865	172329.10	158983.70	231201.10
.6500	.8062	.0483000	.0485098	.0698133	210652.50	211456.20	288862.00
.7000	.8394	.0615600	.0676406	.0919358	252896.30	273979.90	352632.00
.7500	.8705	.0772800	.0925407	.1189457	298664.00	346160.50	421517.20
.8000	.8996	.2970000	.1243853	.1514426	767077.60	426999.40	494376.60
.8500	.9270	.3147000	.1644554	.1900262	783310.90	514987.70	570023.40
.9000	.9528	.3282000	.2141261	.2352892	793119.90	608274.90	647315.20
.9500	.9770	.3391000	.2748517	.2878104	799228.10	704875.60	725221.40
1.0000	1.0000	.3481500	.3481500	.3481500	802868.40	802868.40	802868.40
.0472	.0999	.0002154	.0001461	.0001996	1822.23	1236.28	1688.77
.1003	.1999	.0005122	.0002693	.0004572	4073.73	2144.37	3637.25
.1604	.2948	.0010156	.0005213	.0010049	7434.55	3825.04	7356.62
.2292	.3998	.0024272	.0011723	.0024007	16764.61	8141.77	16583.75
.3084	.4998	.0049816	.0027130	.0054984	31669.08	17403.34	34882.83

Table B-10: 3,5-Dichloroaniline Solubility in Acetone/Water Mixtures

Solvent Mole Frac.	Solvent Volume Frac.	UNIFAC Mole Frac. Sol.	Excess Free Energy Mole Frac. Sol.	Log-linear Mole Frac. Sol.	UNIFAC Sol.	Excess Free Energy Sol.	Log-linear Sol.
[-]	[-]	[-]	[-]	[-]	[mg/l]	[mg/l]	[mg/l]
.0000	.0000	.0000817	.0000872	.0000872	732.27	781.19	781.19
.0500	.1764	.0003692	.0003342	.0004109	2864.52	2593.81	3187.59
.1000	.3114	.0012044	.0014962	.0013459	8219.71	10198.83	9179.88
.1500	.4180	.0031378	.0055975	.0034353	19039.52	33655.87	20821.66
.2000	.5043	.0074060	.0164600	.0073372	40159.52	86711.16	39795.24
.2500	.5756	.0151940	.0387417	.0137361	73784.51	176423.00	66980.15
.3000	.6356	.0288900	.0757249	.0232639	125338.50	294780.60	102337.50
.3500	.6866	.0520800	.1275040	.0364456	200472.80	423610.20	145060.50
.4000	.7307	.5025500	.1908076	.0536718	976937.40	546055.90	193864.80
.4500	.7690	.5143000	.2602438	.0751934	972313.20	652505.90	247290.40
.5000	.8027	.5242000	.3299749	.1011305	966876.90	739828.50	303936.10
.5500	.8326	.5325800	.3950132	.1314890	960805.40	808519.00	362600.30
.6000	.8592	.5398000	.4518601	.1661815	954330.10	860502.70	422340.30
.6500	.8831	.5461000	.4985869	.2050476	947590.90	897992.60	482474.40
.7000	.9047	.5516000	.5345897	.2478731	940626.10	923039.60	542553.30
.7500	.9243	.5564900	.5602209	.2944064	933560.40	937417.10	602318.30
.8000	.9421	.5607300	.5764297	.3443724	926293.30	942637.30	661660.10
.8500	.9584	.5644400	.5844699	.3974837	918897.00	940004.50	720580.90
.9000	.9734	.5676400	.5856907	.4534494	911346.60	930669.00	779165.40
.9500	.9872	.5704900	.5814027	.5119816	903775.30	915665.60	837556.40
1.0000	1.0000	.5728000	.5728000	.5728000	895939.30	895939.30	895939.30
.0266	.1001	.0001914	.0001677	.0002101	1585.29	1388.56	1739.51
.0578	.1998	.0004521	.0004239	.0005046	3435.55	3221.74	3833.39
.0952	.2998	.0010870	.0013029	.0012158	7506.54	8989.14	8391.09
.1406	.3997	.0026577	.0044481	.0029249	16476.74	27388.97	18114.95
.1971	.4997	.0070830	.0155612	.0070491	38655.10	82635.23	38474.54

Table B-11: Aniline Solubility in Methanol/Water Mixtures

Solvent Mole Frac. [-]	Solvent Volume Frac. [-]	UNIFAC Mole Frac. Sol. [-]	Excess Free Energy Mole Frac. Sol. [-]	Log-linear Mole Frac. Sol. [-]	UNIFAC Sol. [mg/l]	Excess Free Energy Sol. [mg/l]	Log-linear Sol. [mg/l]
.0000	.0000	.0110590	.0066620	.0066620	5545.52	33430.00	33430.00
.0500	.1055	.0172169	.0094280	.0113025	78461.61	44183.44	52608.98
.1000	.1993	.0252667	.0135468	.0180887	106426.10	59298.05	77993.89
.1500	.2833	.0353631	.0194627	.0275601	137740.80	79512.74	109859.70
.2000	.3590	.0475984	.0277103	.0402697	171586.20	105490.50	148062.80
.2500	.4275	.0619990	.0389022	.0567653	207111.50	137691.60	192073.40
.3000	.4898	.0785244	.0537133	.0775724	243505.80	176279.80	241063.30
.3500	.5468	.0970695	.0728612	.1031813	280043.90	221075.60	294025.70
.4000	.5990	.1174715	.0970842	.1340363	316115.80	271565.10	349896.70
.4500	.6470	.1395167	.1271191	.1705294	351230.60	326959.90	407659.00
.5000	.6914	.1629487	.1636797	.2129950	385010.70	386292.10	466413.90
.1482	.2805	.0692000	.0192127	.0271662	245574.40	78688.53	108600.50
.1500	.2833	.0686000	.0194627	.0275601	243486.70	79512.74	109859.70
.2000	.3590	.1375000	.0277103	.0402697	399764.10	105490.50	148062.80
.2052	.3665	.1653000	.0287259	.0417996	452162.30	108544.00	152381.50

Table B-12: Aniline Solubility in Ethanol/Water Mixtures

Solvent Mole Frac. [-]	Solvent Volume Frac. [-]	UNIFAC Mole Frac. Sol. [-]	Excess Free Energy Mole Frac. Sol. [-]	Log-linear Mole Frac. Sol. [-]	UNIFAC Sol. [mg/l]	Excess Free Energy Sol. [mg/l]	Log-linear Sol. [mg/l]
.0000	.0000	.0110590	.0066620	.0066620	54545.52	33430.00	33430.00
.0500	.1453	.0294523	.0124878	.0137988	123620.30	55442.07	60990.54
.1000	.2641	.0636084	.0226907	.0250274	223424.90	89260.42	97782.72
.1500	.3631	.1180791	.0387426	.0410941	342889.20	135007.70	142357.80
.2000	.4468	.1956449	.0618342	.0625069	468177.90	190863.80	192659.40
.2500	.5185	.2968152	.0926518	.0895357	588794.80	253680.20	246579.40
.3000	.5806	.4197624	.1313011	.1222394	699264.90	320000.60	302312.80
.3500	.6349	.5605067	.1773568	.1605056	797884.00	386866.10	358502.20
.4000	.6829	.7132159	.2299874	.2040930	884922.90	452172.50	414238.50
.4500	.7255	.8707010	.2881057	.2526693	961395.30	514667.00	468989.30
.0160	.0499	.0202530	.0081415	.0085548	93426.36	39271.06	41200.42
.0402	.1192	.0378900	.0110487	.0121049	157456.40	50234.19	54833.25
.0651	.1836	.0814300	.0150382	.0167201	286619.90	64366.99	71176.57
.0716	.1994	.1275000	.0162694	.0180987	396477.30	68550.41	75815.55
.0843	.2292	.1417000	.0189236	.0210112	420407.30	77322.62	85305.48

Table B-13: Phenanthrene Solubility in Methanol/Water Mixtures

Solvent Mole Frac.	Solvent Volume Frac.	UNIFAC Mole Frac. Sol.	Excess Free Energy Mole Frac. Sol.	Log-linear Mole Frac. Sol.	UNIFAC Sol.	Excess Free Energy Sol.	Log-linear Sol.
[-]	[-]	[-]	[-]	[-]	[mg/l]	[mg/l]	[mg/l]
.0000	.0000	.0000000	.0000003	.0000003	.30	2.89	2.89
.0500	.1055	.0000001	.0000005	.0000008	1.02	5.08	7.71
.1000	.1993	.0000003	.0000011	.0000021	2.98	9.41	18.40
.1500	.2833	.0000010	.0000021	.0000048	7.90	17.71	39.96
.2000	.3590	.0000024	.0000042	.0000101	18.89	33.20	80.16
.2500	.4275	.0000056	.0000081	.0000199	41.93	61.16	150.17
.3000	.4898	.0000121	.0000153	.0000369	87.12	109.94	265.23
.3500	.5468	.0000248	.0000279	.0000647	170.75	192.07	445.07
.4000	.5990	.0000482	.0000494	.0001084	317.94	325.67	714.13
.4500	.6470	.0000893	.0000847	.0001742	565.21	535.76	1101.56
.5000	.6914	.0001585	.0001407	.0002699	963.96	855.73	1640.97
.5500	.7325	.0002704	.0002268	.0004050	1583.47	1328.42	2369.93
.6000	.7707	.0004454	.0003555	.0005904	2513.67	2007.09	3329.26
.6500	.8062	.0007105	.0005426	.0008386	3867.34	2955.87	4562.20
.7000	.8394	.0011003	.0008078	.0011639	5781.20	4249.68	6113.40
.7500	.8705	.0016584	.0011748	.0015815	8415.52	5973.57	8027.90
.8000	.8996	.0024940	.0016719	.0021084	12223.80	8221.45	10350.01
.8500	.9270	.0036100	.0023317	.0027625	17092.26	11094.20	13122.33
.9000	.9528	.0051230	.0031913	.0035626	23425.72	14697.21	16384.74
.9500	.9770	.0071390	.0042922	.0045284	31510.57	19137.48	20173.45
1.0000	1.0000	.0097860	.0056800	.0056800	41659.97	24520.33	24520.33
.0472	.0999	.0000001	.0000005	.0000008	.93	4.91	7.32
.1003	.1999	.0000003	.0000011	.0000021	2.98	9.44	18.49
.1604	.2997	.0000010	.0000025	.0000056	7.98	20.21	46.47
.2292	.3998	.0000040	.0000062	.0000152	30.34	47.56	116.54
.3084	.4998	.0000137	.0000170	.0000407	97.95	120.99	290.31
.4008	.5998	.0000487	.0000499	.0001092	320.96	328.35	719.31
.5099	.6998	.0001767	.0001550	.0002932	1066.55	935.66	1769.00
.6408	.7999	.0006535	.0005030	.0007876	3580.60	2757.76	4312.78
.8005	.8999	.0025034	.0016776	.0021143	12265.64	8246.91	10375.44
.4555	.6521	.0000953	.0000897	.0001831	600.58	564.89	1152.81
.6791	.8258	.0009196	.0006860	.0010176	4903.30	3661.66	5423.40
.8153	.9082	.0027990	.0018549	.0022942	13574.43	9029.35	11148.63
.9310	.9680	.0063060	.0038426	.0041406	28212.43	17344.77	18669.60

Table B-14: Phenanthrene Solubility in Ethanol/Water Mixtures

Solvent Mole Frac.	Solvent Volume Frac.	UNIFAC Mole Frac. Sol.	Excess Free Energy Mole Frac. Sol.	Log-linear Mole Frac. Sol.	UNIFAC Sol.	Excess Free Energy Sol.	Log-linear Sol.
[-]	[-]	[-]	[-]	[-]	[mg/l]	[mg/l]	[mg/l]
.0000	.0000	.0000000	.0000003	.0000003	.30	2.89	2.89
.0500	.1453	.0000002	.0000010	.0000013	1.86	9.09	11.95
.1000	.2641	.0000009	.0000034	.0000047	7.58	27.67	37.79
.1500	.3631	.0000032	.0000102	.0000132	23.73	75.74	97.85
.2000	.4468	.0000089	.0000269	.0000319	60.98	183.37	217.36
.2500	.5185	.0000213	.0000623	.0000677	134.69	394.55	428.27
.3000	.5806	.0000474	.0001293	.0001299	280.24	763.76	766.97
.3500	.6349	.0000852	.0002437	.0002297	472.03	1348.67	1271.29
.4000	.6829	.0001500	.0004230	.0003800	781.49	2201.26	1977.66
.4500	.7255	.0002473	.0006844	.0005942	1216.15	3359.98	2918.55
.5000	.7636	.0003861	.0010429	.0008865	1798.07	4844.83	4120.69
.5500	.7979	.0005762	.0015104	.0012706	2547.53	6655.87	5603.97
.6000	.8289	.0008277	.0020943	.0017597	3482.34	8774.74	7380.97
.6500	.8571	.0011510	.0027976	.0023659	4618.12	11168.26	9457.16
.7000	.8829	.0015567	.0036192	.0030998	5968.44	13792.89	11831.40
.7500	.9065	.0020560	.0045542	.0039710	7545.13	16599.33	14496.72
.8000	.9282	.0027253	.0055949	.0049870	9587.23	19536.47	17441.27
.8500	.9482	.0034810	.0067314	.0061541	11756.70	22554.56	20649.38
.9000	.9667	.0043780	.0079524	.0074768	14214.59	25607.50	24102.39
.9500	.9840	.0054310	.0092460	.0089582	16972.40	28654.18	27779.64
1.0000	1.0000	.0066500	.0106000	.0106000	20025.43	31659.28	31659.28
.0419	.1238	.0000002	.0000008	.0000011	1.44	7.55	9.69
.0716	.1994	.0000004	.0000017	.0000024	3.57	14.86	20.21
.1167	.2991	.0000015	.0000050	.0000068	11.35	39.25	52.96
.1705	.3990	.0000050	.0000155	.0000193	35.66	110.47	137.97
.2357	.4990	.0000168	.0000496	.0000552	108.80	320.54	356.55
.3163	.5991	.0000557	.0001606	.0001577	322.31	928.02	911.36
.4185	.6992	.0001817	.0005093	.0004510	926.54	2592.81	2296.89
.5523	.7994	.0005864	.0015347	.0012907	2586.33	6746.79	5679.19
.7351	.8996	.0018967	.0042641	.0036966	7050.87	15747.03	13672.63
.3836	.6678	.0001256	.0003560	.0003243	667.33	1889.40	1721.60
.6101	.8348	.0008869	.0022267	.0018724	3695.09	9237.38	7776.19
.7864	.9224	.0025427	.0053019	.0046959	9046.77	18727.51	16613.55
.8946	.9648	.0042740	.0078169	.0073264	13935.29	25277.40	23718.29

Table B-15: Xylene Solubility in Methanol/Water Mixtures

Solvent Mole Frac.	Solvent Volume Frac.	UNIFAC Mole Frac. Sol.	Excess Free Energy Mole Frac. Sol.	Log-linear Mole Frac. Sol.	UNIFAC Sol.	Excess Free Energy Sol.	Log-linear Sol.
[-]	[-]	[-]	[-]	[-]	[mg/l]	[mg/l]	[mg/l]
.0000	.0000	.0000177	.0000333	.0000333	103.99	195.62	195.62
.0500	.1055	.0000438	.0000669	.0000988	242.48	369.92	546.29
.1000	.1993	.0000980	.0001376	.0002600	511.90	718.51	1357.12
.1500	.2833	.0002015	.0002824	.0006182	997.00	1397.11	3053.80
.2000	.3590	.0003863	.0005702	.0013489	1815.39	2677.76	6313.10
.2500	.4275	.0006981	.0011228	.0027336	3121.85	5012.47	12123.85
.3000	.4898	.0012210	.0021462	.0051971	5203.75	9114.33	21815.93
.3500	.5468	.0020230	.0039741	.0093466	8227.01	16048.03	37026.61
.4000	.5990	.0032325	.0071257	.0160108	12553.48	27308.72	59572.32
.4500	.6470	.0050040	.0123779	.0262761	18563.37	44850.04	91208.16
.5000	.6914	.0075350	.0208536	.0415180	26696.74	71002.37	133292.30
.5500	.7325	.0110800	.0341222	.0634254	37466.18	108216.50	186427.00
.6000	.7707	.0159550	.0543130	.0940160	51423.95	158598.80	250192.40
.6500	.8062	.0225600	.0842350	.1356443	69175.89	223296.70	323089.70
.7000	.8394	.0450000	.1275014	.1909992	126831.40	301923.20	402742.80
.7500	.8705	.0625000	.1886516	.2630937	164901.00	392296.50	486303.90
.8000	.8996	.0900000	.2732677	.3552468	219069.00	490699.30	570923.30
.8500	.9270	.1500000	.3880804	.4710585	320771.60	592615.70	654140.70
.9000	.9528	.2000000	.5410592	.6143802	388055.70	693652.70	734111.00
.0472	.0999	.0000418	.0000643	.0000933	231.90	356.59	517.46
.1003	.1999	.0000984	.0001382	.0002614	514.08	721.40	1364.12
.1604	.2997	.0002070	.0003274	.0007320	1013.24	1602.06	3575.19
.2292	.3998	.0005494	.0008499	.0020546	2507.57	3874.43	9319.08
.3084	.4998	.0013328	.0023856	.0057568	5635.27	10046.30	23937.45
.4008	.5998	.0032560	.0071907	.0161434	12635.47	27534.15	60002.62
.5099	.6998	.0081480	.0230414	.0452672	28605.06	77417.20	142933.10
.6408	.7999	.0211930	.0778464	.1270383	65594.48	210311.30	309089.80
.8005	.8999	.0950000	.2742542	.3562815	228965.30	491708.80	571766.00
.3576	.5550	.0021773	.0043519	.0101737	8792.34	17437.61	39935.21
.6184	.7841	.0181600	.0640197	.1079163	57481.34	180725.50	276067.10
.8407	.9220	.1250000	.3640919	.4475534	280116.30	573602.70	638862.00
.9033	.9544	.2000000	.5527156	.6249045	387636.50	700198.10	739242.60

Table B-16: Xylene Solubility in Acetone/Water Mixtures

Solvent Mole Frac. [-]	Solvent Volume Frac. [-]	UNIFAC Mole Frac. Sol. [-]	Excess Free Energy Mole Frac. Sol. [-]	Log-linear Mole Frac. Sol. [-]	UNIFAC . Sol. [mg/l]	Excess Free Energy Sol. [mg/l]	Log-linear Sol. [mg/l]
.0000	.0000	.0000177	.0000333	.0000333	103.97	195.62	195.62
.0500	.1764	.0000603	.0001495	.0002052	307.01	761.09	1044.34
.1000	.3114	.0001641	.0007662	.0008252	737.28	3433.68	3697.16
.1500	.4180	.0003797	.0032383	.0024766	1525.70	12879.90	9876.65
.2000	.5043	.0007786	.0106516	.0060310	2827.62	37526.13	21549.67
.2500	.5756	.0014561	.0277985	.0125835	4821.45	85795.70	40422.53
.3000	.6356	.0025369	.0597693	.0233439	7711.89	159270.20	67508.01
.3500	.6866	.0041823	.1098951	.0395218	11738.26	250285.50	102929.10
.4000	.7307	.0066026	.1783794	.0622295	17188.07	346929.10	145994.40
.4500	.7690	.0100744	.2622739	.0924151	24415.62	439364.40	195463.80
.5000	.8027	.0149668	.3564927	.1308257	33867.50	522252.80	249871.40
.5500	.8326	.0217785	.4551634	.1779950	46114.32	593920.20	307799.50
.6000	.8592	.0311917	.5527651	.2342502	61892.82	654713.40	368053.30
.6500	.8831	.0441513	.6448202	.2997295	82159.67	705780.40	429737.30
.7000	.9047	.0619798	.7281607	.3744067	108157.70	748421.00	492260.60
.7500	.9243	.0865494	.8008907	.4581180	141500.20	783814.40	555303.10
.8000	.9421	.1205400	.8621866	.5505885	184272.50	812940.30	618766.90
.8500	.9584	.1678190	.9120377	.6514571	239131.80	836582.40	682728.20
.9000	.9734	.2340221	.9509948	.7602997	309413.20	855360.10	747397.60
.0266	.1001	.000035	.0000699	.0000934	190.63	379.76	507.29
.0578	.1998	.000071	.0001939	.0002611	356.19	966.76	1301.55
.0952	.2998	.000150	.0006590	.0007324	682.71	2988.28	3320.11
.1406	.3997	.000327	.0025171	.0020508	1343.27	10236.71	8354.58
.1971	.4997	.000748	.0100072	.0057543	2735.05	35512.88	20689.80
.2691	.5997	.001864	.0380217	.0161303	5968.57	111127.40	49773.16
.3642	.6998	.005087	.1275534	.0452621	13960.48	277665.30	114428.80
.4953	.7997	.016964	.3473550	.1268488	38474.34	514932.90	244586.40
.6884	.8999	1.000000	.7097207	.3562688	880202.30	739214.10	477701.30
.1364	.3912	.000407	.0022425	.0018804	1685.19	9211.28	7734.05
.1546	.4266	.002021	.0036512	.0027088	7998.21	14364.36	10691.72
.3634	.6991	.014591	.1265194	.0449243	39292.21	276115.80	113765.00
.4783	.7886	.021650	.3147074	.1131061	49708.03	487623.20	225746.50
.5229	.8168	.050920	.4014827	.1513177	106390.70	556478.30	276044.10
.6161	.8672	1.000000	.5831916	.2543259	880202.30	672155.50	387793.80
.6547	.8853	1.000000	.6530637	.3063591	880202.30	710127.90	435585.60

Table B-17: Xylene Solubility in Ethanol/Water Mixtures

Solvent Mole Frac.	Solvent Volume Frac.	UNIFAC Mole Frac. Sol.	Excess Free Energy Mole Frac. Sol.	Log-linear Mole Frac. Sol.	UNIFAC Sol.	Excess Free Energy Sol.	Log-linear Sol.
[-]	[-]	[-]	[-]	[-]	[mg/l]	[mg/l]	[mg/l]
.0000	.0000	.0000177	.0000333	.0000333	103.99	195.62	195.62
.0500	.1453	.0000749	.0001071	.0001490	395.94	565.57	786.79
.1000	.2641	.0002339	.0003265	.0005070	1122.70	1566.10	2430.25
.1500	.3631	.0005834	.0008988	.0014063	2562.51	3942.91	6157.06
.2000	.4468	.0012853	.0022125	.0033330	5198.27	8918.35	13381.23
.2500	.5185	.0024716	.0048979	.0069809	9248.54	18183.78	25743.77
.3000	.5806	.0043430	.0098588	.0132463	15092.02	33709.10	44848.96
.3500	.6349	.0071085	.0182608	.0231971	23007.27	57377.38	71957.99
.4000	.6829	.0109980	.0314772	.0380269	33228.88	90542.98	107730.80
.4500	.7255	.0162530	.0510040	.0590005	45922.18	133674.00	152097.00
.5000	.7636	.0231390	.0783622	.0873988	61224.18	186222.50	204292.30
.5500	.7979	.0319330	.1150017	.1244696	79211.43	246768.30	263038.10
.6000	.8289	.0550000	.1622221	.1713854	125417.40	313361.70	326792.40
.6500	.8571	.0775000	.2211136	.2292125	163968.50	383919.90	393997.30
.7000	.8829	.1000000	.2925221	.2988877	197662.10	456552.50	463264.70
.7500	.9065	.1500000	.3770352	.3812054	269272.90	529752.70	533482.60
.0419	.1238	.0000607	.0000887	.0001193	326.22	476.49	640.68
.0716	.1994	.0001264	.0001752	.0002603	640.12	886.75	1316.99
.1167	.2991	.0003250	.0004636	.0007273	1513.13	2156.86	3380.30
.1705	.3990	.0008181	.0013179	.0020373	3471.65	5581.84	8605.32
.2357	.4990	.0020710	.0039423	.0057132	7920.40	14982.98	21586.05
.3163	.5991	.0051350	.0121567	.0160295	17430.54	40449.76	52760.99
.4185	.6992	.0127700	.0378852	.0450027	37630.55	105347.40	123171.70
.5523	.7994	.0400000	.1169325	.1264030	97541.42	249714.90	265873.00
.7351	.8996	.1250000	.3504551	.3553112	233611.50	507951.20	512511.80
.2612	.6579	.0028240	.0236907	.0293791	12785.63	98700.99	119794.40
.4026	.6852	.0112350	.0323238	.0389550	33825.50	92540.64	109830.00
.4968	.7613	.0226430	.0763481	.0853345	60162.04	182601.10	200740.10
.5779	.8156	.0475000	.1399707	.1493635	111762.20	283316.40	298097.30
.6072	.8331	.0600000	.1699605	.1790166	134893.50	323325.40	336292.50
.6354	.8492	.0675000	.2026562	.2111413	146646.00	363024.50	374103.10
.6955	.8806	.1000000	.2855656	.2921099	198264.60	449973.00	456977.30
.7705	.9156	1.000000	.4155590	.4187651	880202.30	559667.60	562350.20
.8047	.9301	1.000000	.4848886	.4865014	880202.30	609242.90	610452.30
.7977	.9272	1.000000	.4701825	.4721148	880202.30	599136.80	600618.40
.8357	.9426	1.000000	.5532041	.5534883	880202.30	653701.10	653894.40
.9013	.9672	1.000000	.7147806	.7131453	880202.30	745976.10	745062.60

Table B-18: Xylene Solubility in Propanol/Water Mixtures

Solvent Mole Frac. [-]	Solvent Volume Frac. [-]	UNIFAC Mole Frac. Sol. [-]	Excess Free Energy Mole Frac. Sol. [-]	Log-linear Mole Frac. Sol. [-]	UNIFAC Sol. [mg/1]	Excess Free Energy Sol. [mg/1]	Log-linear Sol. [mg/1]
.0000	.0000	.0000177	.0000333	.0000333	103.99	195.62	195.62
.0500	.1735	.0001076	.0001601	.0001992	549.93	817.57	1017.39
.1000	.3071	.0004055	.0006436	.0007897	1831.07	2903.73	3560.70
.1500	.4131	.0011387	.0020804	.0023560	4600.53	8376.79	9477.21
.2000	.4993	.0025805	.0055199	.0057290	9412.17	19948.43	20690.81
.2500	.5707	.0050480	.0124245	.0119666	16737.14	40366.48	38927.34
.3000	.6309	.0088650	.0244727	.0222561	26862.41	71409.52	65285.12
.3500	.6823	.0143440	.0432913	.0376063	39895.35	113225.10	100009.90
.4000	.7267	.0217690	.0702183	.0597522	55779.16	164364.60	142528.20
.4500	.7655	.0400000	.1061557	.0890854	93329.70	222388.00	191679.00
.5000	.7996	.0575000	.1515224	.1266124	123534.40	284623.90	246023.70
.5500	.8298	.0800000	.2062847	.1729366	158457.50	348740.00	304126.80
.6000	.8568	.0800000	.2700343	.2284593	151438.60	413009.70	364745.50
.6500	.8811	.1500000	.3420840	.2933924	251621.10	476335.90	426923.20
.0270	.0997	.0000505	.0000789	.0000930	274.59	428.73	505.58
.0588	.1995	.0001399	.0002077	.0002604	698.61	1036.88	1299.71
.0967	.2992	.0003956	.0005912	.0007282	1800.03	2687.90	3309.34
.1427	.3990	.0009804	.0017759	.0020374	4023.57	7267.23	8329.15
.1998	.4990	.0025730	.0055003	.0057106	9388.51	19886.14	20632.95
.2725	.5991	.0065800	.0171081	.0160224	20938.09	52971.22	49748.03
.1917	.4861	.0022786	.0047524	.0050015	8448.87	17482.30	18383.82
.4201	.7429	.0300000	.0835477	.0706065	73807.15	187015.00	161567.60
.5960	.8547	.1000000	.2646184	.2236727	185305.50	407892.00	359827.80
.6971	.9018	1.000000	.4167671	.3632086	880202.30	534608.90	486331.30

Appendix C

ERROR ANALYSIS FOR THE PREDICTION OF SOLUTE SOLUBILITY IN CO-SOLVENT/WATER SYSTEMS

Table C-1: Error Analysis for Naphthalene Solubility in Methanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.10	59.00	33.11	-0.251	47.01	-0.099	67.76	0.060
0.20	135.00	75.83	-0.250	80.32	-0.226	149.73	0.045
0.29	243.00	151.70	-0.205	142.97	-0.230	310.63	0.107
0.40	463.00	403.64	-0.060	308.01	-0.177	722.38	0.193
0.50	1230.00	939.94	-0.117	676.00	-0.260	1573.73	0.107
0.49	986.30	378.09	-0.416	618.62	-0.203	1446.32	0.166
0.62	2956.02	2680.83	-0.042	1928.56	-0.185	4058.10	0.138
0.71	6362.04	8267.22	0.114	4102.44	-0.191	7672.79	0.081
0.75	9961.19	10923.72	0.040	6128.26	-0.211	10640.50	0.029
0.84	19831.08	18701.93	-0.025	15036.16	-0.120	21600.38	0.037
0.92	36590.70	37818.34	0.014	32248.37	-0.055	38665.52	0.024
1.00	70556.86	71586.50	0.006	64257.14	-0.041	64758.33	-0.037
1.00	71093.43	72746.55	0.010	65377.12	-0.036	65595.64	-0.035

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	81.1	69.8	118
Accuracy	148	149	125

Number of Points = 13

Table C-2: Error Analysis for Naphthalene Solubility in Acetone/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.10	111.00	28.86	-0.576	62.25	-0.251	81.88	-0.132
0.20	418.00	59.04	-0.849	169.42	-0.392	216.99	-0.285
0.30	1076.00	124.67	-0.936	566.60	-0.279	572.31	-0.274
0.40	3539.00	271.46	-1.115	2112.19	-0.224	1492.19	-0.375
0.50	10194.00	614.63	-1.220	8021.32	-0.104	3848.23	-0.423
0.55	23006.55	953.56	-1.382	15562.54	-0.170	6236.90	-0.567
0.62	40209.35	1750.25	-1.361	35873.58	-0.050	11883.48	-0.529
0.68	72889.01	3149.76	-1.364	69197.59	-0.023	20887.11	-0.543
0.71	106553.50	4027.69	-1.423	87882.03	-0.084	26218.75	-0.609
0.77	134162.00	7110.94	-1.276	138813.50	0.015	42958.41	-0.495
0.80	164479.00	10690.71	-1.187	174782.90	0.026	57945.71	-0.453
0.83	196467.00	15886.97	-1.092	209417.00	0.028	76769.38	-0.408
0.87	234097.00	23806.16	-0.993	239393.50	0.010	99623.70	-0.371

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	8.34	76.7	38.0
Accuracy	1325	149	275

Number of Points = 13

Table C-3: Error Analysis for Naphthalene Solubility in Ethanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.35	370.00	305.84	-0.083	399.87	0.034	586.00	0.200
0.39	981.00	450.86	-0.338	586.51	-0.223	842.72	-0.066
0.45	1510.00	699.65	-0.334	975.62	-0.190	1350.57	-0.048
0.44	1895.00	796.21	-0.377	841.76	-0.352	1170.48	-0.209
0.54	3951.00	1426.09	-0.443	2192.58	-0.256	2802.79	-0.149
0.64	9853.00	3258.43	-0.481	5774.13	-0.232	6620.10	-0.173
0.70	13821.00	4972.19	-0.444	9503.83	-0.163	10317.38	-0.127
0.79	23653.00	10048.80	-0.372	20821.92	-0.055	21018.14	-0.051
0.86	36400.00	16980.26	-0.331	36583.27	0.002	35739.49	-0.008
0.98	76588.00	42446.46	-0.256	85819.80	0.049	84959.86	0.045
1.00	95116.73	48310.11	-0.294	95166.72	0.000	95166.72	0.000

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	45.6	74.8	88.5
Accuracy	227	152	132

Number of Points = 11

Table C-4: Error Analysis for Naphthalene Solubility in Propanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.28	991.00	193.47	-0.709	295.49	-0.526	339.36	-0.465
0.32	2003.00	278.33	-0.857	432.49	-0.666	481.90	-0.619
0.40	4063.00	538.16	-0.878	887.24	-0.661	918.09	-0.646
0.51	9996.00	1397.98	-0.854	2625.20	-0.581	2382.16	-0.623
0.65	19938.00	4325.33	-0.664	9628.46	-0.316	7591.44	-0.419
0.76	30839.00	10329.17	-0.475	24216.22	-0.105	18294.27	-0.227
0.88	74325.00	24207.25	-0.487	53309.67	-0.144	42822.42	-0.239
0.94	113061.00	38680.04	-0.466	75305.15	-0.176	66215.20	-0.232

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	21.2	40.1	36.8
Accuracy	495	285	132

Number of Points = 8

Table C-5: Error Analysis for Naphthol Solubility in Methanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.00	845.90	1367.50	0.209	845.27	0.000	845.27	0.000
0.10	1283.00	2620.27	0.310	1202.34	-0.028	1619.56	0.101
0.20	2655.00	4903.62	0.266	1869.71	-0.152	3091.91	0.066
0.30	5104.00	8072.99	0.199	3143.46	-0.211	5871.45	0.061
0.40	9086.00	16448.31	0.258	5661.64	-0.205	11096.72	0.087
0.50	16788.00	29268.96	0.241	10774.56	-0.193	20776.85	0.093

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	177	73.9	117
Accuracy	178	144	119

Number of Points = 6

Table C-6: Error Analysis for Naphthol Solubility in Acetone/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.00	845.90	1367.50	0.209	845.27	0.000	845.27	0.000
0.10	2109.60	2855.90	0.132	1359.75	-0.191	1675.63	-0.100
0.20	3653.30	6142.49	0.226	2872.76	-0.104	3289.25	-0.046
0.30	6419.10	13563.86	0.325	7314.78	0.057	6413.70	0.000
0.40	14948.00	30769.84	0.314	20347.10	0.134	12350.15	-0.083
0.50	71163.00	95013.48	0.126	56111.40	-0.103	23453.76	-0.482

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	167	92.4	76.1
Accuracy	172	130	160

Number of Points = 6

Table C-7: Error Analysis for Quinoline Solubility in Methanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.00	6760.00	3874.71	-0.242	6832.62	0.005	6832.62	0.005
0.10	9872.00	8788.05	-0.051	10047.33	0.008	12861.90	0.115
0.20	19231.00	19175.61	-0.001	15915.14	-0.082	24043.24	0.097
0.30	32840.00	36549.58	0.046	26835.63	-0.088	44442.00	0.131
0.40	71567.00	89503.40	0.097	47619.57	-0.177	80909.25	0.053
0.50	105925.00	123049.20	0.065	87273.59	-0.084	143448.40	0.132

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	96.8	85.2	123
Accuracy	130	124	126

Number of Points = 6

Table C-8: Error Analysis for Quinoline Solubility in Acetone/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.10	14603.00	7779.03	-0.274	10673.41	-0.136	12605.04	-0.064
0.20	34048.00	15829.47	-0.333	21111.05	-0.208	22969.19	-0.171
0.30	75378.00	33679.62	-0.350	48618.28	-0.190	41372.56	-0.261
0.40	125493.00	76713.59	-0.214	117552.30	-0.028	73060.05	-0.235
0.50	251189.00	210232.90	-0.077	266766.90	0.026	125827.90	-0.300

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	56.3	78.1	62.2
Accuracy	186	138	167

Number of Points = 5

Table C-9: Error Analysis for 3,5-Dichloroaniline Solubility in Methanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.00	692.00	732.27	0.025	781.19	0.053	781.19	0.053
0.10	1108.00	1822.23	0.216	1310.28	0.073	1789.81	0.208
0.20	2301.00	4073.73	0.248	2399.61	0.018	4069.70	0.248
0.30	3423.00	7434.55	0.337	4506.32	0.119	8663.40	0.403
0.40	7689.00	16764.61	0.339	10148.03	0.121	20642.87	0.429
0.50	13964.00	31669.08	0.356	22855.78	0.214	45653.98	0.514

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	179	125	203
Accuracy	189	131	221

Number of Points = 6

Table C-10: Error Analysis for 3,5-Dichloroaniline Solubility in Acetone/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.10	1551.00	1585.29	0.009	1393.32	-0.047	1745.47	0.051
0.20	2191.00	3435.55	0.195	3231.67	0.169	3845.21	0.244
0.30	3876.00	7506.54	0.287	9013.68	0.367	8414.01	0.337
0.40	8879.00	16476.74	0.269	27453.70	0.490	18158.00	0.311
0.50	21004.00	38655.10	0.265	82797.10	0.596	38552.01	0.264

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	160	206	174
Accuracy	170	246	183

Number of Points = 5

Table C-11: Error Analysis for Aniline Solubility in Methanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.28	81131.00	136564.40	0.226	78688.53	-0.013	108600.50	0.127
0.37	168783.00	175217.00	0.016	108544.00	-0.192	152381.50	-0.044
0.45	414731.70	217610.60	-0.280	148226.00	-0.447	205810.10	-0.304

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	97.1	60.6	84.4
Accuracy	161	191	156

Number of Points = 3

Table C-12: Error Analysis for Aniline Solubility in Ethanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.05	33684.00	93426.36	0.443	39271.06	0.067	41200.42	0.087
0.12	43070.00	157456.40	0.563	50234.19	0.067	54833.25	0.105
0.18	50295.00	286619.90	0.756	64366.99	0.107	71176.57	0.151
0.23	63534.00	420407.30	0.821	77322.62	0.085	85305.48	0.128

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	442	122	132
Accuracy	460	121	132

Number of Points = 4

Table C-13: Error Analysis for Phenanthrene Solubility in Methanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.00	2.90	0.30	-0.985	2.89	-0.002	2.89	-0.002
0.65	1036.00	600.58	-0.237	494.65	-0.321	1009.51	-0.011
0.83	5133.00	4903.30	-0.020	3426.72	-0.175	5075.90	-0.005
0.91	10150.03	13574.43	0.126	8720.44	-0.066	10767.86	0.026
0.97	17786.99	28212.43	0.200	17136.88	-0.016	18446.07	0.016
1.00	24520.33	41659.97	0.230	24520.33	0.000	24520.33	0.000

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	76.9	80.0	101
Accuracy	272	142	103

Number of Points = 6

Table C-14: Error Analysis for Phenanthrene Solubility in Ethanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.67	2404.00	667.33	-0.557	1664.61	-0.160	1516.75	-0.200
0.83	10317.00	3695.09	-0.446	8676.59	-0.075	7303.60	-0.150
0.92	17124.00	9046.77	-0.277	18188.32	0.026	16134.48	-0.026
0.96	22663.00	13935.29	-0.211	24946.03	0.042	23407.00	0.014
1.00	31659.28	20025.43	-0.199	31659.28	0.000	31659.28	0.000

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	45.9	92.6	84.6
Accuracy	232	121	130

Number of Points = 5

Table C-15: Error Analysis for Xylene Solubility in Methanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.00	196.00	103.99	-0.275	195.62	-0.001	195.62	-0.001
0.55	8839.00	8792.34	-0.002	17437.61	0.295	39935.21	0.655
0.92	217688.00	58471.34	-0.571	573602.70	0.421	638862.00	0.468
0.95	428636.00	387636.50	-0.044	700198.10	0.213	739242.60	0.237
0.97	697318.00	880202.30	0.101	765734.20	0.041	790482.70	0.054

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	69.5	156	192
Accuracy	194	178	238

Number of Points = 5

Table C-16: Error Analysis for Xylene Solubility in Acetone/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.39	3938.00	1685.19	-0.369	9211.28	0.369	7734.05	0.293
0.43	4813.00	7998.21	0.221	14364.36	0.475	10691.72	0.347
0.87	179336.00	880202.30	0.691	672155.50	0.574	387793.80	0.335
0.89	186956.00	880202.30	0.673	710127.90	0.580	435585.60	0.367

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	201	316	217
Accuracy	337	321	217

Number of Points = 4

Table C-17: Error Analysis for Xylene Solubility in Ethanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.66	10912.10	12785.63	0.069	98700.99	0.956	119794.40	1.041
0.69	56531.00	33825.50	-0.223	92540.64	0.214	109830.00	0.288
0.76	112270.00	60162.04	-0.271	182601.10	0.211	200740.10	0.252
0.82	197255.00	111762.20	-0.247	283316.40	0.157	298097.30	0.179
0.83	236654.00	134893.50	-0.244	323325.40	0.136	336292.50	0.153
0.85	285539.00	146646.00	-0.289	363024.50	0.104	374103.10	0.117
0.88	490114.00	298264.60	-0.216	449973.00	-0.037	456977.30	-0.030
0.92	663875.00	880202.30	0.122	559667.60	-0.074	562350.20	-0.072
0.93	716126.00	880202.30	0.090	609242.90	-0.070	610452.30	-0.069
0.93	753712.00	880202.30	0.067	599136.80	-0.100	600618.40	-0.099
0.94	786326.00	880202.30	0.049	653701.10	-0.080	653894.40	-0.080
0.97	809721.00	880202.30	0.036	745976.10	-0.036	745062.60	-0.036

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	81.6	130	137
Accuracy	153	200	215

Number of Points = 12

Table C-18: Error Analysis for Xylene Solubility in Propanol/Water System

Solvent [% Vol.]	Experiment [mg/l]	UNIFAC [mg/l]	Error	Free Energy [mg/l]	Error	Log Linear [mg/l]	Error
0.49	37964.00	8448.87	-0.653	17482.30	-0.337	18383.82	-0.315
0.74	148648.00	73807.15	-0.304	187015.00	0.100	161567.60	0.036
0.85	312010.00	185305.50	-0.226	407892.00	0.116	359827.80	0.062
0.90	548198.00	880202.30	0.206	534608.90	-0.011	486331.30	-0.052

	UNIFAC [%]	Excess Free Energy [%]	Log-Linear [%]
Bias	57.0	92.7	85.7
Accuracy	246	153	146

Number of Points = 4

Appendix D

Physical Characteristics of Soils

Characteristics of soils

Three soils were used in this study. Several soil physical characteristics were evaluated

Particle Size Analysis Soil particle size is one of the most apparent physical characteristics of a soil, and particle size provides a description of the soil's physical "make-up" or textural composition. This determination gives the relative proportions of the varying size fractions which comprise the soil mass. Soil particle sizes greater than 0.074 mm are generally analyzed by sieving methods, while finer particles, i.e. particle size smaller than 0.074 mm or particles passing through a U.S. standard sieve No. 200, are analyzed by gravity sedimentation using a hydrometer. Particle size analysis was performed according to procedures described by Lambe (1951).

The sieve analysis does not determine individual particle sizes; rather it determines the percentage of soil particle sizes in a range of diameters. This is accomplished by adding distilled water to the soil sample (approximately 500 g) and working it into a slurry, then washing the slurry through a U.S. No. 200 sieve. This is followed by oven-drying the soil retained on the No. 200 sieve and performing the sieve analysis. The sieve analysis is accomplished by passing a quantity of soil (approximately 100 g) through a series of sieves. The soil is shaken mechanically and sieved for fifteen minutes. The quantity of soil retained by each sieve is expressed as percentage of the total mass of soil sample. The results of the sieve analysis for the three soils are presented in Table D-1.

Table D-1: Sieve Analysis of Soils

Sieve No. [#]	Particle Diameter [mm]	Percent Retained [%]	Percent Pass. [%]
Hagerstown			
10	2.00	0.0	100.00
20	0.84	2.65	97.35
40	0.42	4.81	90.19
60	0.25	14.01	85.99
100	0.149	18.43	81.57
140	0.015	20.61	79.59
200	0.074	24.97	75.03
bottom	< 0.074	100	0.00
Berkeley			
10	2.00	0.00	100.00
20	0.84	1.36	98.64
40	0.42	4.86	95.14
60	0.25	7.84	92.16
100	0.149	11.61	88.39
140	0.105	13.46	80.54
200	0.074	16.99	83.01
bottom	< 0.074	100.00	0.00
Tifton			
10	2.00	0.00	100
20	0.84	21.88	78.12
40	0.42	54.00	46.00
60	0.25	72.27	27.73
100	0.149	84.91	15.09
140	0.105	87.30	12.70
200	0.074	92.42	7.58
bottom	< 0.074	100	0.00

Hydrometric techniques are used to determine particle size for particles passing through the No. 200 sieve. These procedures consist of carefully washing the suspension into a 1000 ml graduated cylinder, adding dispersant, filling to the 1000 ml mark with deionized water, and then thoroughly mixing the suspension for approximately 30 seconds. This is followed by inserting a calibrated hydrometer in the suspension, and taking hydrometer readings at total elapsed times of 1/4, 1/2 and 1 and 2 minutes. After two minutes, the hydrometer is removed and the suspension is re-mixed and the test is performed again, but no readings are taken until two minutes have elapsed. For this reading and subsequent readings, the hydrometer is inserted just prior to measurement. Hydrometer readings are taken at increasing time intervals (e.g. 2, 5, 10, 20, minutes etc.) until the hydrometer reading is close to 1.001. After the final reading, the suspension is poured into an evaporating dish and oven-dried, followed by weighing the soil to 0.1 g.

The particle size distribution of an assembly of soil particles is expressed as percent finer by weight. Lambe (1951) defined sand as consisting of small rock particles that vary in size from 0.05 mm to 1.0 mm, with silt comprising fine particles of size 0.002 to 0.05 mm, and clay describing fine inorganic particles of less than 0.002 mm in size. Using these definitions for sand, silt and clay, the composition of the three soils used in this study is shown in Table D-2. These compositions may be compared to the U.S. Department of Agriculture Textural Classification scheme (Casagrande, 1948), for which Hagerstown soil is classified as silt loam, Berkeley soil is classified as silt loam, and Tifton soil is classified as sand.

Specific Gravity Analysis Specific gravity of a soil refers to the mean density of the soil particles collectively. It is expressed as the ratio of the weight in air of a given volume of soil to the weight in air of an equal volume of distilled water at a temperature of 4 °C. A pycnometer is normally used to measure specific gravity of soil. In this study, a 250 ml

Table D-2: Classification of Soils

	Sand	Silt	Clay
Hagerstown	48%	32%	20%
Berkeley	15%	57%	28%
Tifton	90%	7%	3%

Hagerstown	Silt loam
Berkeley	Silt loam
Tifton	Sand

Sand: 0.05 mm < d < 2.0mm

Silt: 0.002 < d < 0.05 mm

Clay: d < 0.002 mm

volumetric flask was used for this measurement rather than a customary 1000 ml pycnometer because the soil sample was large enough to compensate for any decrease in precision in measuring fluid volume.

The specific gravity test gives the dry weight density. This test was conducted by placing 50 g of oven-dried soil in a 250 ml volumetric flask. Care was taken to clean the outside and neck of the flask where soil may be deposited during transfer, and then the flask was filled approximately one-half full with deionized water. Entrapped air was removed by gently boiling the water for several minutes. The flask was then cooled to room temperature and filled with degassed, deionized water. The flask was then weighed and the temperature was measured. Lastly, the soil solution was removed from the flask, and the flask was then filled with degassed, deionized water at the same temperature and weighed. The specific gravity of the soil was calculated as follows:

$$G_s = \frac{W_s \, G_T}{W_s - W_1 + W_2}$$

where W_s is the dry weight of soil, G_T is the specific of water at the temperature, W_1 is the weight of flask, soil and water, and W_2 is the weight of flask and water. The specific gravity for Hagerstown silt loam was measured as 2.63, Berkeley silt loam was measured as 2.61, and Tifton sand was measured as 2.60.